# Sunday Afternoon, October 19, 2008

## Biomaterials Plenary
## Room: 202 - Session BP-SuA

### Bio-inspired Catalysis, Energy Production and Transduction: Opportunities and Challenges
**Moderator:** B. Kasemo, Chalmers University of Technology, Sweden

3:00pm **BP-SuA1 From Nature and Back Again...Giving New Life to Materials for Energy, Electronics and the Environment**, ***A.M. Belcher***, Massachusetts Institute of Technology **INVITED**

Termites and their complex hindgut microbiota are able to convert wood lignocellulose into hydrogen and other products used to fuel their metabolisms. Recent gene and genome based analyses on the gut community have revealed novel insights into many bacteria-mediated, important symbiotic functions. The system-wide gene analysis of a microbial community specialized towards plant lignocellulose degradation has both basic and applied implications.

3:40pm **BP-SuA3 Artificial Photosynthesis and Bio-Inspired Chemistry: Combining Technology with Biology for Efficient Solar Energy Conversion**, ***T. Moore***, *A.L. Moore, M. Hambourger, D. Gust*, Arizona State University **INVITED**

Provided significant challenges can be met, solar powered, bio-inspired constructs can contribute to renewable energy resources to meet human energy needs. The central challenge is using renewable energy sources to reverse the combustion process by efficient water oxidation and reductive synthesis of $CO_2$ to fuels. Nature's catalysts direct these oxidation/reduction reactions along coordinates that have low activation barriers and almost no side reactions. In principle, these reactions can be driven by electricity provided by sustainable sources. In order to accomplish this, it will be necessary to switch nature's catalysts from their usual source of redox potential - electron/proton carrying redox species - to emf at appropriate electrical potentials. Taking a step in this direction, we have assembled a hybrid system in which a porphyrin-sensitized Grätzel-type nanoparticulate wide band gap semiconductor photoanode is used as an interface between emf and redox potential for the photochemical reformation of biomass to hydrogen.

4:20pm **BP-SuA5 Bioelectrocatalysis in Diabetes Management**, ***A. Heller***, University of Texas at Austin **INVITED**

FreeStyle NavigatorTM, introduced this year by Abbott Diabetes Care, accurately monitors minute by minute the glucose concentration in the subcutaneous fluid. The system alerts the diabetic user to actual and impending high and low glucose levels. It is intended to eliminate the constant worry of diabetic people about their having or not having the desired level of glucose. The system was approved for use in the 27 countries of the European Union in 2007 and by the FDA in 2008. The sensor of Navigator, implanted in the fat under the skin at 5 mm depth, is the first and only one having a bioelectrocatalyst at which glucose is directly electrooxidized. The bioelectrocatalyst is a thick-film of a water-swollen redox polymer, which 3-dimensionally envelopes and penetrates the glycoprotein of the enzyme glucose oxidase, forming a unique crosslinked hydrated network in which electrons, glucose, and ions diffuse. Electrons cascade across small potential gradients from glucose to the reaction centers of the enzyme; from the enzyme to the hydrated redox polymer; and through the hydrated polymer to the anode of a miniature electrochemical cell. Navigator follows FreeStyle, the first mass manufactured sub-microliter fluidic device, introduced in 2000 and available worldwide, which made the monitoring of glucose in withdrawn blood samples painless. Its core is a 300 nL thin-layer microcoulometer, in which glucose is electrooxidized in a two-step process diffusionally mediated by PQQ-glucose dehydrogenase and a complex of osmium.

## IPF 2008 Frontiers in Imaging: from Cosmos to Nano
## Room: 312 - Session IPF-SuA

### Astronomical Imaging
**Moderator:** L. Hartmann, University of Michigan

3:00pm **IPF-SuA1 Large Telescope Projects**, ***R. Bernstein***, University of California, Santa Cruz **INVITED**

Over the last 150 years, the diameter of the largest operating telescope has doubled every 30 years. The last generation of telescopes (6-10 m diameters) have been in scientific operation for about a decade. While those projects faced a number of optical and structural challenges, the success of the next generation of telescopes depends not only on conquering the technological challenges that come with scaling up large structures, but also on controlling costs and achieving new standards in image quality through active controls and adaptive optics. In this talk, I will discuss some of the challenges associated with building and operating the next generation of "Extremely Large" Telescopes (ELTs).

3:40pm **IPF-SuA3 Instrumentation for Large Telescopes**, ***D. Fabricant***, Harvard-Smithsonian **INVITED**

In the past 25 years, the application of new technologies has transformed instrumentation for large, ground-based telescopes. These technologies include the development of large optical and infrared array detectors, newly available large crystalline and optical glass lens materials, and high speed robotics. Harnessing these technologies requires a high level of sophistication in engineering and applied physics, including optical, thermal, structural, and control system design. I describe state-of-the-art instruments for imaging and spectroscopy now operating at large telescopes, and look forward to our plans for the next generation of extremely large telescopes.

4:20pm **IPF-SuA5 Adaptive Optics in Astronomy**, ***B.L. Ellerbroek***, TMT Observatory Corporation **INVITED**

Adaptive optics (AO) is a technology for the real-time correction of the optical aberrations experienced by light waves as they propagate through atmospheric turbulence and similar distorting media. AO is now used at numerous ground based astronomical observatories, and currently obtains (for many applications) image quality which approaches what could be achieved with the same aperture diameter in space. The benefits of AO increase dramatically with telescope size; for the future generation of extremely large telescopes, the benefits of AO may be as great as 100 times larger than can be obtained with existing telescopes on account of the factor of 10 advantage in collecting area. In this presentation, we will briefly review the fundamentals of adaptive optics, illustrate some of the astronomical results which have been achieved using AO to date, summarize the recent advances in component technologies and system concepts which enable the implementation of AO on future extremely large telescope, and finally, describe the designs and expected performance of the "first light" AO systems for the Thirty Meter Telescope project.

5:00pm **IPF-SuA7 Imaging with Near-infrared Interferometers**, ***J.D. Monnier***, University of Michigan **INVITED**

Under the best conditions, telescope diffraction limits the angular resolution for astronomical imaging. Using interferometry, we can coherently combine light from widely-separated telescopes to overcome the single-telescope diffraction limit to boost our imaging resolution by orders of magnitude. I will review recent technical advances combining four telescopes of the CHARA Array on Mt. Wilson, CA, with baselines of 330 meters allowing imaging with sub-milli-arcsecond resolution. I will present the first resolved images of main sequence stars besides the Sun and show first results imaging interacting binary systems.

## 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 nanoprobes 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 nanoprobes, 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. Grennberg*, 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 $H_2$, $O_2$, $CO_2$, CO and $H_2O$ 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 Polyvinylidenefluoride 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 cyclicvoltammetry (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., Chemi. 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. Gölzhäuser***, 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 posses 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. Gölzhäuser: Free-standing nanosheets from cross-linked biphenyl self-assembled monolayers, Adv. Mat., 17, 2583-2587, (2005)

[2] A. Turchanin, M. El-Desawy, A. Gölzhäuser: 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. Gölzhäuser: 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 $CH_4/H_2$ gas mixture have been previously reported. When $C_2H_2/H_2$ 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 $C_2H_2$ nanosheets were deposited on Si substrates using 80% $C_2H_2$ diluted in $H_2$ gas (5 sccm total gas flow rate) at 600 ºC 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 $C_2H_2$ nanosheets yielded a threshold field, for an emission current density of 10 $\mu A/cm^2$, of ~3 V/µm, which was ~2 V/µm lower than $CH_4$ nanosheets. At an applied field of 5.3 V/µm, the current density was 1.1 $mA/cm^2$ compared to the $CH_4$ nanosheets of ~0.007 $mA/cm^2$. Calculations from the Fowler-Nordheim plots and their linear fits indicated that the effective emission area of $C_2H_2$ nanosheets was ~15 times that of $CH_4$ nanosheets and the $\beta$ factor of $C_2H_2$ nanosheets was ~26% higher than $CH_4$ nanosheets. The results are consistent with the morphology differences between the two kinds of nanosheets. The lifetime tests of $C_2H_2$ nanosheets conducted in a DC mode with a base pressure lower than $5\times10^{-9}$ 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 $N_2/O_2$ Addition to $C_2F_6/H_2$ Gases,** ***W. Takeuchi,*** Nagoya University, Japan, *M. Hiramatsu,* Meji 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 $C_2F_6$ gas with H radical injection. The influences of $N_2$ and $N_2/O_2$ addition to $C_2F_6/H_2$ 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 $N_2/O_2$ 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 $N_2$ addition. In the case of $N_2$ 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 $N_2$ addition on the atomic composition of CNWs. The carrier and N concentration in the CNW films formed by $N_2/O_2$ mixture gas addition were almost the same as those in the CNW film by $N_2$ 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 spectroscopy[2] 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 $CH_4$, $H_2$, Ar. Typical flow rate of $CH_4$, $H_2$ 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.

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

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

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

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

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

## IPF 2008 Frontiers in Imaging: from Cosmos to Nano
## Room: 312 - Session IPF-MoM

### Bio-Imaging
### **Moderator:** J. Hollenhorst, Agilent Technologies

8:20am **IPF-MoM1 Trapping Single Molecules in Water at Room Temperature,** ***A.E. Cohen***, Harvard University **INVITED**

To study a single molecule, one would like to hold the molecule still, without perturbing its internal dynamics. I will present a machine that achieves this goal. The Anti-Brownian Electrokinetic trap (ABEL trap) tracks the Brownian motion of a single molecule using fluorescence microscopy, and applies electrical kicks to the molecule that are timed to induce an electrokinetic drift that cancels the Brownian motion.[1] The ABEL trap can immobilize single biomolecules for extended observation and has been used to study the dynamics of individual DNA molecules and protein chaperonins.[2] I will give examples of new things that can be learned from trapped molecules.[3]

[1] A. E. Cohen and W. E. Moerner, “Suppressing Brownian motion of individual biomolecules in solution,” Proc. Natl. Acad. Sci. USA 103, 4362-4365 (2006).

[2] A. E. Cohen and W. E. Moerner, “Principal Components Analysis of shape fluctuations of single DNA molecules,” Proc. Natl. Acad. Sci. USA 104, 12622-12627 (2007).

[3] A. E. Cohen and W. E. Moerner, “Controlling Brownian motion of single protein molecules and single fluorophores in aqueous buffer,” Opt. Express 16, 6941-6956 (2008).

9:00am **IPF-MoM3 Pushing Magnetic Resonance Imaging Into the Nanoscale Regime - the Quest for a Molecular Structure Microscope,** ***D. Rugar***, IBM Research Division **INVITED**

I describe our effort to extend magnetic resonance imaging (MRI) into the nanometer regime using a technique called magnetic resonance force microscopy (MRFM). MRFM achieves a billion-fold improvement in the sensitivity of magnetic resonance detection by replacing the conventional inductive pickup with ultrasensitive detection of magnetic force. This increase in sensitivity can be harnessed to greatly improve the resolution of magnetic resonance microscopy. In a series of recent experiments at IBM, we have successfully demonstrated 3D magnetic resonance imaging with spatial resolution on the order of 5 nm. The experiment operates in field gradients up to 50 gauss per nanometer (5 million tesla per meter) and makes use of the naturally occurring statistical polarization of nanoscale ensembles of nuclear spins. Understanding the unusual point spread function of MRFM is key to converting the measured 3D force map into a real-space image of the proton distribution in the sample. As a first demonstration of 3D nanoscale MRI, we have imaged individual tobacco mosaic virus particles. The long term goal of this work is to develop a "molecular structure microscope" whereby one could directly image the 3D atomic structure of macromolecules.

10:20am **IPF-MoM7 Imaging in Cell Biology,** ***T. Kirchhausen***, Harvard Medical School **INVITED**

11:00am **IPF-MoM9 Intracellular Fluorescence Imaging at Nanometer Resolution,** ***H.F. Hess***, Howard Hughes Medical Institiute **INVITED**

Fluorescence microscopy, is usually limited in its ability to resolve and focus on features smaller than the optical diffraction limit. However special photoactivated fluorescent proteins can be harnessed in a technique called Photo-Activated Localization Microscopy, PALM. Successive sparse subsets of these fluorescent proteins can be activated, imaged, individual molecules localized and their coordinates accumulated and rendered into a PALM image. Thereby the distribution of labeled endogenous proteins can be seen with the resolution of an electron microscope. PALM images of protein location and organization are illustrated with mitochondria, lysosomes, actin networks, focal adhesions and other cell structures. Another technique, an interferometric microscope, is described that can measure the vertical position of fluorescent molecules to nanometer precision with high photon efficiency. This can be combined with PALM to give full 3 dimensional molecular coordinates of proteins with ~ 20 nm resolution.

11:40am **IPF-MoM11 Retinal Imaging with MEMS-based Adaptive Optics,** ***S. Olivier***, Lawrence Livermore National Laboratory **INVITED**

## MEMS and NEMS
## Room: 206 - Session MN-MoM

## Integrative Materials and Processes for MEMS/NEMS
## Moderator: E. Gousev, Qualcomm

8:20am **MN-MoM1 Integrated Piezoelectric RF MEMS Front-Ends,** ***G. Piazza***, University of Pennsylvania **INVITED**

This paper reports on the work performed in Dr. Piazza's laboratory for the realization of integrated piezoelectric RF MEMS front-ends. The work deals with three different aspects of the concept of MEMS integration: (i) integration of different piezoelectric devices such as resonators, filters and switches to create single-chip RF signal processors; (ii) integration of dissimilar materials such as thin film diamond and AlN piezoelectric films to enhance device quality factor and raise frequency of operation of resonators and (iii) integration or, more appropriately, considerations for integration with state-of-the-art CMOS electronics. The fundamental challenges faced from material, fabrication and design perspectives to attain the aforementioned three levels of integration are highlighted. For example, stress control, material and processing compatibility are important components that need to be taken into account in the demonstration of AlN switched filter banks. Surface roughness and etching compatibilities pose limitation in the fabrication of thin film diamond/AlN micromechanical resonators and constrain the design space. Furthermore, the material stack, deposition temperature and etching techniques need to be selected so that they are compatible or available in CMOS foundries. Design and experimental results demonstrating, for the first time, switched piezoelectric resonators and initial steps towards the integration of thin film diamond/AlN resonators are presented. These preliminary demonstrations set the foundations for the development of new classes of devices that can disrupt the way we currently perform RF signal processing by enabling fast frequency hopping and low power frequency synthesis in a broad frequency spectrum that could not be previously covered by any other MEMS technology.

9:00am **MN-MoM3 Chemically-Modified Graphene Nanomechanical Resonators,** ***M.K. Zalalutdinov***, SFA Inc., *J.T. Robinson, E.S. Snow, Z. Wei, P.E. Sheehan, J.W. Baldwin, B.H. Houston*, Naval Research Laboratory

High quality factor (Q~4000) radio frequency (20-100 MHz) nanomechanical resonators are fabricated using suspended ultra-thin films of chemically modified graphene (CMG).[1] The films were prepared by spin-casting graphene oxide platelets onto $SiO_2$/Si substrates, reducing back toward graphene using chemical and/or thermal treatments, then lifting-off and transferring films to patterned substrates. Large-area continuous films can be deposited using this method, enabling batch fabrication of nanoelectromechanical devices. Membranes as thin as 4 nm can be successfully transferred and suspended over 2.7 µm diameter holes. The ability to withstand high in-plane tensile stress (T~10 N/m, deduced from membrane resonant frequencies) as well as high quality factors show that the integrity of the film is NOT compromised by the inter-platelet bonding. The extremely small mass of these CMG resonators provides an estimate for the added mass sensitivity as low as $\delta m\sim10^{-18}$ g. In-plane stress inherent to as-fabricated CMG membranes can be dynamically tuned over a wide range due to thermoelastic effects by applying a low power localized heat source. In conjunction with the short thermal relaxation time ($\tau\sim10^{-8}$ sec) this enables techniques such as parametric pumping for further enhancement of the performance of CMG resonators. Thicker (h>15 nm) suspended CMG films show similar quality factors, can withstand strain in excess of 0.3% and constitute a virtually unpenetrateable barrier for water or vapor as confirmed by resonant frequency measurements. Membranes encapsulating water on one side and exposed to vacuum on the other side show no frequency dependence on a time scale of days, indicating perfect sealing. In addition, both the membranes themselves and the adhesion of the CMG film to the substrate are strong enough to withstand boiling of the encapsulated water ($T_{anneal}>100°C$). Finally, ultra-thin CMG films are optically transparent and feature only minor e-beam scattering thereby facilitating access to encapsulated objects for imaging and/or spectroscopy. We will describe mechanical and thermomechanical properties of CMG films extracted from the behavior of the nanoresonators and discuss possible applications in sensing and nanofluidics.

This work was supported by the Office of Naval Research.

[1] Ruoff, R. Nature Nanotechnology 3, 10-11 (2008).

9:20am **MN-MoM4 Electrical Transduction of Multi-layer Polysilicon Resonators,** ***J.D. Cross***, *B.R. Ilic*, Cornell University, *M.K. Zalalutdinov*, SFA Inc., *E. Yilmaz*, Cornell University, *J.W. Baldwin, B.H. Houston*, Naval Research Laboratory, *H.G. Craighead, J.M. Parpia*, Cornell University

A straightforward means of electrical transduction of resonator motion is investigated using MHz-frequency micromechanical resonators made from multi-layer film stacks. Devices are fabricated using polysilicon films stacked on top of each other with intermediate layers of insulating material. Electrical or optical drive is used to induce motion in the resonators and electrical transduction allows for direct detection of the resonator motion. A variety of structure geometries are investigated, including cantilevers, double-clamped beams, mushrooms, and domes. Quality factors of 1000-10000 are routinely observed. We discuss the transduction mechanism as well as the ability to integrate these kinds of MEMS structures into a standard CMOS foundry process with no added or modified fabrication steps. We show that the multi-layer film stack can be delaminated in the release step, resulting in stacked resonator structures with thin gaps between each vibrating surface. This work was partially supported by the Office of Naval Research, DARPA, and fabrication was performed at the Cornell NanoScale Science and Technology Facility.

9:40am **MN-MoM5 Selective Detachment of Microspheres using In-Plane Modes of Nanoelectromechanical Oscillators,** ***B.R. Ilic***, Cornell University, *S. Krylov*, Tel Aviv University, Israel, *M. Kondratovich, H.G. Craighead*, Cornell University

Manipulating dynamics of flexural and torsional vibrational modes of micro- and nanoelectromechanical systems (MEMS and NEMS) with external fields has long been a sought-after goal. A widely studied class of NEMS devices consists of surface micromachined mechanical oscillators made of thin film layers patterned into various shapes that operate by motion perpendicular to the plane of the thin film and substrate by bending in their thin direction. Conventional mechanical driving and motion transduction methods typically activate and detect only motion in this "out-of-plane", transverse direction. We previously demonstrated a robust method for driving and detecting the motion of micro- and nano-scale resonators by utilizing optical drive of resonant motion and interferometric detection of that motion by a separate laser. This technique allowed non-invasive activation and interrogation of individual oscillators or arrays of oscillators. We describe here an approach that can activate and detect the perpendicular, in-plane motion of such oscillators. We show that optical fields are efficient for excitation, direct control and measurement of in-plane motion of cantilever-type nanomechanical oscillators. Using optical excitation and interferrometric detection, we dynamically analyzed surface micromachined 200nm and 250nm thick single crystal silicon cantilevers of varying lengths and widths. We also have demonstrated the controlled capture, detection and release of submicrometer particles by the application of forces imparted by the in-plane motion of the resonators. In contrast, the out of plane motion, even in the strong non-linear impact regime, was insufficient for the removal of bound polystyrene spheres. Our results suggest that optical excitation of in-plane mechanical modes provide a unique mechanism for controlled removal of particles bound on the surface of nanomechanical oscillators.

10:20am **MN-MoM7 Synthesis and Characterization of Large Area Ultrananocrystalline Diamond (UNCD) Films using Microwave Plasma Chemical Vapor Deposition Process and Integration with CMOS**, ***A.V. Sumant***, *O. Auciello,* Argonne National Laboratory*, V. Adiga, A. Konicek,* University of Pennsylvania*, X. Zhong, B. Kabius,* Argonne National Laboratory*, H. Yuan, Z. Ma,* University of Wisconsin-Madison*, R. Carpick*, University of Pennsylvania

Because of exceptional mechanical, chemical, electrical and tribological properties of ultrananocrystalline diamond (UNCD), it has great potential to be used in for the development of high-performance, harsh environment-compatible devices for MEMS and NEMS, such as resonators and switches. Recent work by our group has demonstrated fabrication of functional RF-MEMS switches and resonators based on UNCD. However, transition of this technology to the industry will critically depend on the ability to produce UNCD films on wafer scale with acceptable thickness and microstructure uniformity. We have achieved 4%, 7%, and 11% uniformity in UNCD film thickness across 100 mm, 150 mm, and 200 mm diameter Silicon substrates respectively using 2.45 GHz and 915 MHz microwave plasma chemical vapor deposition (MPCVD) process. All the films were grown in the temperature range of 400-800 oC. We report on the microstructure uniformity, phase, and impurity content of UNCD films by using atomic force microscopy (AFM), Near edge X-ray absorption fine structure spectroscopy (NEXAFS), and forward recoil spectrometry (FRES) characterization techniques respectively. Additionally, we have developed a materials integration strategy to enable diamond-CMOS integration. Ultrananocrystalline diamond (UNCD), a novel material developed in thin film form at Argonne, is the only diamond film that can be grown at 400oC, and still retain exceptional mechanical, chemical, and tribological properties comparable to that of single crystal diamond. We have developed a process based on microwave plasma CVD to synthesize UNCD films on 150 and 200 mm CMOS wafers, which will open new avenues for building CMOS-driven devices for MEMS/NEMS based on UNCD. UNCD films were grown successfully on individual Si-based CMOS chips and on 200 mm CMOS wafers at 400 oC in a microwave-plasma-enhanced chemical vapor deposition (MPCVD) system with Ar-rich/CH4 gas mixture. The CMOS devices on the wafers were characterized before and after UNCD deposition. All devices were performing to specifications with acceptable degradation after UNCD deposition and processing. A threshold voltage degradation in the range of 0.08-0.44V and transconductance degradation in the range of 1.5-17% were observed. We also report the on the cross-section TEM/EELS studies of the UNCD/CMOS interface and discuss the possible mechanisms responsible for the degradation of CMOS performance.

10:40am **MN-MoM8 {100}-Textured PZT Films Grown on Chemically Deposited $PbTiO_3$ Seed Layers for MEMS Applications**, *J. Zhong,* ***S. Kotru****, H. Han, R.K. Pandey*, The University of Alabama

Lead zirconate titanate (PZT)-based thin films are gaining increased interest in wide variety of applications in MEMS due to their large longitudinal and transverse piezoelectric coefficients, and the compatibility with microelectronic circuits. Both micro-machined sensors (such as accelerometer and gyroscope) and actuators (such as micro-motors, micro-pumps, and micro-switches) have been fabricated based on PZT films. The piezoelectric response of PZT films is the key factor for sensing and actuation function of a device; the higher the value, the better the device will act as sensor and/or actuator. Texture of the films plays a major role in determining the piezoelectric response. So far, the highest transverse piezoelectric coefficient (-12.0 $C/m^2$) has been reported for {100}-textured PZT films grown on $PbTiO_3$ seed layers. These $PbTiO_3$ were sputtered at 500~600° C. High temperature sputtering limits the practical implementation of such films in MEMS devices due to process constraint and sample size limitations. In this work, highly {100}-textured PZT films have been grown with $PbTiO_3$ seed layers. However, the seed layers in our work were deposited by chemical solution deposition. The effect of both Pb content and solution concentration of $PbTiO_3$ on PZT films was investigated extensively. These PZT films show 97% of {100} texture and effective transverse piezoelectric coefficients of -13.3 $C/m^2$. Thus our films have higher effective transverse piezoelectric coefficient than the PZT films grown with sputtered $PbTiO_3$ seed layers. Our approach of obtaining {100}-textured PZT films with high piezoelectric response on chemically deposited seed layers has advantage of being much easy and low-cost. Such films are feasible for MEMS based device implementation.

11:00am **MN-MoM9 Suppression of Anelastic Effects in Micromechanical Resonators from Suspended Al-CNT Nanolaminate Thin-Films**, ***Y.D. Kim****, J.H. Bak, S.W. Cho, B.Y. Lee, S.R. Lee, K. Char, S. Hong, Y.D. Park*, Seoul National University, South Korea

We present evidence that the addition of Al-CNT lamina to suspended Al thin-film micromechanical resonators suppress anelastic effects. Addition of Al-CNT lamina to form a metallic-CNT nanolaminate has been shown to enhance mechanical properties, including elastic modulus as well as strengths, from dynamic and quasi-static flexural measurements of suspended doubly-clamped micromechanical beam resonator structures.[1] In this study, dynamic flexural measurements for long loading-cycles ($>10^{11}$) is presented. The micromechanical beam resonator structures, which are patterned by a combination of e-beam and photolithography methods, are fabricated from UHV sputter deposition of Al onto a self-assembled CNT network on a GaAs substrate, which is selectively removed to suspend the beam. The frequency response of the microresonators is periodically measured by a laser vibrometer-like set-up, while the beam is actuated electrostatically. For Al beam resonators, the resonance frequency ($f_o$), which is directly related to the its elastic modulus, varies during the duration of measurement ($\Delta f_o / f_o < 1.5\%$), while for Al-CNT beam resonators, $f_o$ is relatively unchanged for the duration. Such observations is consistent with the view that the CNTs mechanically reinforce and is well-incorporated in the Al thin-film, as anelastic effects are attributed to grain boundary sliding and are a contributor to stress relaxation in metallic thin-films.[2]

[1] J.H. Bak, Y.D.Kim et al., Nature Materials advance online publication, 20 April 2008 (doi:10.1038/nmat2181).

[2] S. Hyun et al., Appl. Phys. Lett. 87, 061902 (2005).

11:20am **MN-MoM10 An Opto-Thermo-Mechanical MEMS Sensor for Direct Thermal Imaging**, *P. Apte,* ***B. Seth****, O. Karhade, S. Chiluveru*, IIT Bombay, India

Infrared imaging plays a critical role in many applications ranging from night vision, environmental monitoring and astronomy. The paper describes a room-temperature compensated opto-thermo-mechanical un-cooled infrared imaging system with a direct color display. The sensor consists of an array of sensing elements suspended from the substrate using bimorph beam elements. Infrared radiation incident on a sensing element is absorbed and leads to a rise in temperature. The heat conducted from the sensing element to the bimorph beam elements leads to a deformation of the beam elements and results in a displacement of the sensing element in a direction perpendicular to the plane of the sensing element. Thus the lateral positions of the sensing elements is influenced by the infrared energy received by the sensing elements in addition to the room temperature. The lateral movement of sensing element is converted into a color image by interference of reflected light from the sensing element and another parallel element with an air gap suitable for creating a constructive interference in the visible spectral range. This second parallel element is also mounted using similar bimorph beam elements and is made of a material transparent to infrared radiation. Thus the transverse position of the transparent element does not depend on the incident infrared radiation but only the ambient temperature. This way it is possible to cancel the effect of room temperature on the interference pattern. The design considerations for the above device are described here. Various configurations of arranging the elements and the bimorph are discussed along with their relative merits. Simulations were conducted using Ansys© software. For an incident radiation of 100 $W/m^2$, the rise in temperature of 0.3mm x 0.3mm sensing element was about 5 degrees C. The sensitivity of the device was found to be of the order of 4 $nm^3/W$. The time constant of the device was found to be about 2 seconds.

11:40am **MN-MoM11 An Optical MEMS Sensor for Catechol Detection**, ***P.H. Dykstra****, J. Hao, S.T. Koev,* University of Maryland*, G.F. Payne,* University of Maryland Biotechnology Institute (UMBI)*, L. Yu, R. Ghodssi*, University of Maryland

Catechol is a widely studied phenol which is a common byproduct of factory waste. Its presence in drinking water and food poses a safety concern due to its toxic and possibly carcinogenic effects. We report the successful fabrication and testing of an optical MEMS sensor for the detection of catechol. Other reported sensors suffer from a lack of selectivity. This sensor marks the first time optical measurements have been utilized for catechol detection on chip. In addition, it provides improved selectivity over conventional detection methods. Typically used detection techniques involve electrochemically oxidizing catechol solution and measuring the current from the reaction over time. However, these methods are prone to false positives since any other easily oxidized chemicals present, such as ascorbic or citric acid, will create a current. Other studies involving catechol detection have shown that byproducts from catechol oxidation will induce a significant absorbance change in an aminopolysaccharide film of chitosan. Chitosan is derived from the biopolymer chitin and has been well characterized by our group in the past. This absorbance change in chitosan caused by catechol oxidation is shown to be the highest in the UV and near UV range of the spectrum. Our reported device takes advantage of this unique absorbance property to detect catechol by measuring the change in light intensity at 472 nm. The device consists of a single microfluidic channel patterned in SU-8 with perpendicular waveguides for guiding light through a deposited chitosan film. Indium Tin Oxide (ITO), a transparent conductor, is used as the cathode on the waveguide facet to facilitate the chitosan film deposition. Chitosan forms a solid film at pH higher than 6.3 which allows it to be selectively deposited onto a cathode during an electrochemical reaction. As catechol flows down the channel it is electrochemically oxidized via patterned electrodes and causes the absorbance change in the chitosan film. Blue laser light is coupled in and out of the device using multimode optical fibers and the intensity is measured by an external spectrophotometer. The higher concentration of catechol contributes to a higher absorbance as expected while oxidizing buffer solution and ascorbic acid display no measurable change in the absorbance through the chitosan film. The data displays a considerable response even for the lowest measured concentration (0.001 M).

## 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 µm$^2$ SRAM Cell Exposed with EUV Lithography**, ***J.-F. de Marneffe**, D. Goossens, A. Vandervorst, S. Demuynck, 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 µm$^2$ 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 $Si_3N_4$ as an etch-stop liner, covered by 240nm $SiO_2$. 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, $SiO_2$ followed by $Si_3N_4$ etch, residue cleaning) leading to the successful patterning of small contacts by EUV lithography.

[1] Imaging Performance of the EUV Alpha Demo Tool at IMEC, G.F. Lorusso et al., SPIE conference 6921-24 (2008).

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. Passemard, 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 $SiO_2$ 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 $SiO_2$ 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 realisation 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 $SiO_2$ 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 $SiO_2$ material, the air cavities present a spherical profile because the HF chemistry removes isotropically the $SiO_2$ 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$_x$O$_y$) layers on the walls of trenches and vias in interconnects. These MnSi$_x$O$_y$ layers were found to be excellent barriers to diffusion of Cu, oxygen and water. The adhesion of Cu to MnSi$_x$O$_y$ was also found to be sufficiently strong to satisfy the semiconductor industry requirements. The MnSi$_x$O$_y$ 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$_x$O$_y$ 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$_x$O$_y$ layer that is strongly adherent to the Cu. These capping MnSi$_x$O$_y$ 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 (HfO$_2$)$_x$(SiO$_2$)$_{1-x}$ 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 Si$^{+4}$ and Hf$^{+4}$ 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.

## Plasma Science and Technology
## Room: 304 - Session PS-MoM

## Plasma Etching for Advanced Interconnects
**Moderator:** K. Bera, Applied Materials, Inc.

8:20am **PS-MoM1 Comparison Between Hybrid and Porous Dielectric Material (SiOCH) Integration Strategies for Interconnect Technologies*, J. Ducote*,** STMicroelectronics, France*, T. David, N. Posseme,* CEA-LETI-MINATEC, France*, T. Chevolleau,* CNRS-LTM, France*, S. Gall, A. Zenasni, V. Jousseaume,* CEA-LETI-MINATEC, France*, R.-L. Inglebert,* UJF-LTM, France*, C. Verove,* STMicroelectronics, France*, O. Joubert*, CNRS-LTM, France

To reduce interconnect RC delays in the future, porous SiOCH materials (p-SiOCH) are introduced as low dielectric constant materials. However, the porosity brings serious issues such as an increased sensitivity to etch and ash plasma exposures generating significant changes in the film structural properties. These issues can be aggravated by the integration strategy. One interesting emerging solutions is the late porogen removal process in which the porosity is generated by a sacrificial carbon based porogen desorbed after patterning or chemical-mechanical polishing (CMP) steps. Such hybrid materials (SiOCH matrix and porogen) are expected to be less sensitive to plasma induced damages similarly than dense low k materials. Starting from a standard damascene integration scheme, we investigate the advantages and drawbacks of hybrid materials (h-SiOCH) compared to porous materials. Etch mechanisms in fluorocarbon (FC) plasmas, material modifications induced by etching, post etch wet cleans and CMP processes are studied. Experimental results show that etching must proceed in low polymerizing chemistries since both ellipsometry and X-ray photoelectron spectroscopy (XPS) indicate an increased fluorine and carbon concentrations on the surface and lower etch rates than with porous materials. These results are well correlated with the dense nature and the high carbon content of the hybrid material both attributed to the presence of porogens. After conventional post etch wet cleans (fluorhydric acid based), no modification of the hybrid material has been evidenced thanks to infrared analyses. The impact of CMP using Hg probe measurement and IR spectroscopy has also been studied. While porous materials are modified during CMP processes due to surfactant diffusion of the slurry trough the pores, no modification is observed with hybrid materials. We have finally performed a full metal integration process and investigated the impact of the porogen removal process on the copper lines integrity. Preliminary experiment shows that copper lines are impacted by the thermally UV-assisted treatment that generates copper line corrosion issues. A promising solution, that will be presented in this paper, consist in protecting the Cu lines by a CoWP self-aligned barrier deposition and a siliciuration-nitridation process.

8:40am **PS-MoM2 Etching Characteristics of Low-k SiOCH Films by Fluorocarbon Beams: Molecular Dynamics Study*, A. Suzuki*,** *M. Isobe,* Osaka University, Japan*, S. Kobayashi, M. Fukasawa, T. Tatsumi,* Sony Corp., Japan*, S. Hamaguchi*, Osaka University, Japan

Highly accurate control of plasma etching processes of low-dielectric-constant (i.e., low-k) insulating materials for interconnects of semiconductor chips has become increasingly important as the dimensions of transistors and interconnect wires in planer technologies diminish. In this work, in an attempt to clarify etching characteristics of SiOCH films, which are widely used as low-k materials for interconnect insulator, we have studied interaction of SiOCH films with impinging fluorocarbon beams, using molecular dynamics (MD) simulations. The simulation code and interatomic potential functions for Si, O, C, F, and H atoms are the same as those used in Ref. 1. In the simulation study presented here, we have first created model SiOCH films by depositing various monomers consisting of Si, O, C, and H atoms with low incident energies. In the numerical process of film deposition, film properties such as density, atomic composition, and porosity vary greatly, depending on the conditions used in the process. The numerical deposition processes used here were not intended to simulate actual SiOCH film formation processes but simply used to prepare model substrates that are similar to porous SiOCH films used in actual semiconductor chip manufacturing. In etching simulations, the injection energies examined in this work have been 100, 200, and 300eV. Unlike SiO2, which has the sputtering yield threshold energy at around 250eV for CF3 ion injections, numerically obtained sputtering yields for SiOCH films are significantly higher. For example, the numerically obtained Si sputtering yield (defined here as the number of Si atoms removed from the substrate surface per injection) by CF3 injections at 100eV is about 0.48. The sputtering yields for SiOCH films have been also confirmed to be an increasing function of the incident energy. We have also examined the sputtering yield dependence on (1) the film density and also (2) incident beam species varying from F to CFx with x = 1~4. For the latter, at 100eV, the dependence on the value x is found to be rather weak.

[1] T. Takizawa, et al., AVS 54th International Symposium & Exhibition, October 14-19, 2007, PS1-MoM2.

9:00am **PS-MoM3 Plasma Challenges of Porous SiOCH Patterning for Advanced Interconnect Levels**, ***T. Chevolleau***, CNRS/LTM France, *T. David, N. Posseme,* CEA/LETI/D2NT France, *M. Darnon,* CNRS/LTM France, *F. Bailly,* CEA/LETI/D2NT France, *R. Bouyssou,* CNRS/LTM France, *J. Ducote,* CEA/LETI/D2NT France, *L. Vallier, O. Joubert*, CNRS/LTM France **INVITED**

In CMOS technology, one of the dominant strategies to achieve future generation of ultra low-k interlayer dielectric (ILD) materials with a dielectric constant close to 2.2 is to introduce porosity into a SiOCH matrix. For the integration of porous SiOCH in damascene structures, the most important challenges are: 1) to manage profile control of narrow features (sub-75 nm trenches and vias), 2) to minimize the plasma-induced damages (modification and surface roughness) and 3) to prevent barrier diffusion into the porous SiOCH. In this work, we will address the damages (modification and surface roughness) induced by the etching and ashing plasmas on both blanket and patterned wafers. The film modification and surface roughness induced by fluorocarbon, reducing, and oxidizing plasmas have been characterized by using infrared spectroscopy, ellipsometry, atomic force microscopy techniques. The results will be presented and discussed in terms of mechanisms of film modification and formation of surface roughness. Experiments will also focus on the profile control of narrow p-SiOCH trenches using different masking strategies (metal hard mask versus organic mask). Plasma etching conditions have been optimized for both type of mask approaches to achieve sub-75 nm patterns using scanning electron microscopy and chemical topography analyses by X-ray photoelectron spectroscopy. We have shown that the organic hard mask exhibits better patterning capability in terms of trench profile control. The use of metallic hard mask can lead to profile distortion and process drift induced by metal contamination on the patterned structures and on the reactor walls of the etcher, respectively. Post etching treatments like reducing ($NH_3$, $H_2$/He, $CH_4$…) and oxidizing ($O_2$) plasmas have also been investigated on both blanket and patterned wafer to limit the barrier diffusion. We have shown that the barrier diffusion can be strongly limited if the ashing plasma generates a modification and densification of the p-SiOCH material surface. In conclusion, a delicate trade-off has to be found between the modification of the porous SiOCH film and the limitation of the barrier diffusion in order to minimize the increase in k value.

9:40am **PS-MoM5 Plasma Damages on Organic Low-k Film due to VUV Radiation, UV Radiation, Radicals, Radicals with Radiation, and Ions in $H_2$/$N_2$ Plasma Etching Processes**, ***K. Takeda***, *S. Takashima, R. Saito, S. Uchida,* Nagoya University, Japan, *M. Fukasawa, K. Oshima, K. Nagahata, T. Tatsumi,* Sony Corporation, Japan, *M. Hori*, Nagoya University and JST-CREST, Japan

The low dielectric constant (low-k) films are widely introduced as interlayer dielectrics for ULSIs. An organic low-k film, polyallylene (PAr), is one of prospective candidates for interlayer films with low-k. PAr receives the damages from the plasmas. The plasma damages induce the increase of the dielectric constant of the films. In our previous studies, we have developed the novel technique for evaluating the damages due to radiation, radicals and ions in plasmas separately (Pallet for plasma evaluation : PAPE) and clarified the generation mechanism of porous SiOCH films using the PAPE in plasma etching using $H_2$ and $N_2$ gases.[1] In this technique, a vacuum ultraviolet (VUV) window, an ultraviolet (UV) window, a Si plate, or nothing were placed on low-k films and were irradiated by plasmas. Therefore, we can evaluate the influence of individual VUV radiation, UV radiation, radicals, radicals with radiations, and ions on the damage of films. In this study, the damage induced by $H_2$/$N_2$ plasma was investigated to clarify the generation mechanism of surface changes due to VUV radiation, UV radiation, radicals, radicals with radiation, and ions on the organic low-k films. The dual frequency capacitively coupled plasma apparatus for 8 inch wafer processing was used in this study. VHF (60MHz) and bias (2MHz) powers of 500 W were applied to the upper and the bottom electrodes, respectively. The pressure of $H_2$ and $N_2$ mixture gas was 5.3 Pa. The etching time was 20 s. At a gas flow rate ratio of 50 %, the etching depth of the sample irradiated by radiation, radicals, and ions was approximately 80 nm. The other samples on the conditions without ion bombardment were not etched and the refractive index of the sample irradiated by radiation, radicals, and ions increased significantly compared to the other samples, which indicated that the damages caused by ions were greater than those due to VUV, UV radiation, and radicals. On the other hand, in the pure $N_2$ plasma, the thicknesses and refractive indexes of all samples were not changed. From these results, the damage caused by the ion bombardment was suppressed by surface nitriding of organic low-k film due to $N_2$ plasma exposure. On the basis of results, the generation mechanism of damage is presented.

[1] S. Uchida, S. Takashima, M. Fukasawa, K. Ohshima, K. Nagahata, T. Tatsumi , and M. Hori, J. Appl. Phys., 103 (2008) 073303.

10:20am **PS-MoM7 Impact of Reducing and Oxidizing Post Etching Plasma Treatments on Porous SiOCH Integration**, ***R. Bouyssou***, *T. Chevolleau,* CNRS-LTM, France, *T. David, N. Posseme,* CEA-LETI-MINATEC, France, *J. Ducote,* STMicroelectronics, France, *L. Vallier, J. Joubert*, CNRS-LTM, France

For 45 nm interconnect technology node and beyond, porous SiOCH (p-SiOCH) materials with porosity higher than 25% and a dielectric constant lower than to 2.5 are being introduced. However the porosity brings serious integration issues such as a high sensitivity of porous materials to etching and ashing plasma exposures and the risk of metallic precursor diffusion into the dielectric during conformal barrier deposition. This work focuses on the development of post etching plasma treatments using reducing and oxidizing chemistries. Such plasma treatments can be used as i) ashing processes and/or ii) post cleaning processes (wafer and/or reactor walls) and/or iii) "pore sealing-like" processes to prevent metal barrier diffusion. p-SiOCH wafers (porosity of 26% and k=2.35) prepared by plasma enhanced chemical vapour deposition have been etched and post etched in a dual frequency capacitive reactor. Plasma induced modifications of p-SiOCH have been investigated both on blanket and patterned wafers using volume and surface analyses techniques such as infrared spectroscopy (in transmission and in multiple internal reflexion), ellipsometry (spectroscopic and porosimetric), x-ray photoelectron spectroscopy and water contact angle. For each chemistry ($NH_3$, $H_2$, $CH_4$ and $O_2$), we have optimized the plasma conditions minimizing the p-SiOCH modifications such as carbon depletion, new bonds formation (Si-H, Si-OH,..) and moisture uptake. After methane based plasma treatments ($CH_4$/$N_2$) a carbon rich layer (a few nanometers thick) presenting hydrophobic properties is deposited on the p-SiOCH surfaces. After $NH_3$ and $O_2$ based plasmas, the surface becomes hydrophilic and carbon free. Infrared analyses show no moisture uptake after $CH_4$ based plasmas while a significant amount of water uptake is detected after $NH_3$ and $O_2$ plasmas. Furthermore, dielectric constant (k) measurements after the different plasma treatments demonstrate that the k increase is strongly related to the formation of silanol groups and moisture uptake. The capabilities of the plasma treatments presented in this study to remove post etch-residues from the p-SiOCH surface and to prevent the barrier diffusion into p-SiOCH will be also addressed.

10:40am **PS-MoM8 Effects of Plasma Etch and Ash Processes on Porous Low-k Film Surfaces in a Dual-Damascene Flow**, ***C.B. Labelle***, Advanced Micro Devices, Inc., *D. Horak,* IBM Research, *Y. Zhou, A. Li, K. Zhou, C. Zhang, R. Patz, A. Darlak, J. Pender*, Applied Materials, Inc.

Porous ultra low k dielectrics (k < 2.4) are being integrated into current and future technology nodes. As film dielectric values are driven lower, new interactions are observed between the films and the plasma etch environments to which they are exposed. Some of these interactions are extensions of the chemical sensitivities previously observed for k=2.4 materials (i.e., plasma ash damage), while others are a result of the change in the microstructure of the films as additional porosity is incorporated to decrease dielectric constant (i.e., pore size, pore connectivity, etc.). Post-etch and ash film surface roughness has often been observed with porous dielectrics and the etching and ashing process window to achieve a smooth dielectric surface decreases as the porosity increases. In this work, post-etch and/or ash film surface roughness effects will be examined for several different structures. The focus of the work is on a k=2.2 porous carbon doped oxide film utilizing a via first trench last integration scheme. Surface roughness phenomena are observed both on planar and vertical surfaces. In some cases, plasma modification to the film from one step is only observed several steps beyond the damage point. The sensitivity of the film requires careful control of every step of every plasma exposure to minimize cumulative and/or combinatory effects. Results will be presented highlighting some of the process spaces explored. This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:00am **PS-MoM9 Mechanisms of Residue Formation on TiN Hard Mask after Patterning of Porous SiOCH Films in Fluorocarbon-Based Plasma**, ***N. Posseme***, CEA-LETI, France, *T. Chevolleau, R. Bouyssou,* LTM-CNRS, France, *T. David,* CEA-LETI, France, *V. Arnal, N. Jourdan, S. Doloy, C. Verove,* ST Microelectronics, France, *O. Joubert*, LTM-CNRS, France

For the 45 nm interconnect technology node, the introduction of porous SiOCH materials (p-SiOCH) brings major concerns such as the sidewall modifications induced by ashing plasmas used to strip the photoresist. Metallic hard mask (MHM) integration avoids exposure of the porous SiOCH films to resist stripping plasmas but generates its own set of issues such as metal contamination of the patterned structures. In particular, the growth of metallic residues on the MHM is often observed after p-SiOCH etching in fluorocarbon (FC) plasmas. Since, these defects are not removed after wet cleans, they directly impact the electrical performance measured on via chains. This work focuses on the mechanisms of residue formation on metallic hard mask (titanium nitride, TiN deposited by Physical Vapor Deposition) when exposed to FC based plasma etching. In situ post-etch plasma treatments have also been investigated as potential solution to remove these defects. The mechanisms of residue formation have been investigated using different analyses techniques such as ex-situ x-ray photoelectron spectroscopy (XPS), scanning electron microscopy cross section and energy dispersive x-ray (EDX). These experiments have been performed on TiN blanket wafers deposited on 200 nm thick $SiO_2$ layers and on patterned wafers etched in a dual frequency capacitive etcher. The growth of residues on metallic hard mask is observed when the wafer is etched in FC plasmas and exposed to air. EDX and XPS analyses both show that these residues are $TiF_x$ like residues. We have also observed that the kinetic of residue formation after air exposure on metal hard mask is correlated with the etching chemistry ($SF_6$, $C_xF_y$, ...), the plasma operating conditions (w or w/o ion bombardment), the chemical composition of the etched materials ($SiO_2$, p-SiOCH, SiCN) and moisture content. Based on these results, the mechanisms of the residues formation will be presented and discussed.

11:20am **PS-MoM10 BEOL Pattern Flop Over as a Challenge to Shrink Feature Critical Dimension Continuously**, ***Y. Yin****, J.C. Arnold,* IBM Corporation*, T. Sparks,* Freescale Corporation*, P. Basler, S. Schmitz*, IBM Corporation

As feature critical dimension (CD) shrinks toward the limit of Moore's law, many problems, including pattern flop over, become serious challenges in the Back-End-Of-Line (BEOL) plasma etch development. A clear understanding of the origin and control of pattern flop over is extremely desirable since it will cause failure in product development. BEOL pattern flop over is due to several different reasons. One of the root causes is the high Aspect Ratio (AR) of mask/dielectric lines. As the technology node moves from one generation to the next, the feature pitch size shrinks faster than the feature vertical dimension (trench/via depth) to allow the integration density to increase. Consequently, mask/dielectric lines with higher AR in BEOL are required. When the AR exceeds the critical value (approximately 3) flop over can happen very easily. The mask/dielectrics lines bend over and sometimes touch each other. Different flop over phenomena have already been observed at 22 nm node look-ahead research. Photoresist feature delamination has been noted post resist development because of the smaller pitch size. Two of the most significant mechanisms, mask flop over and dielectrics flop over, occur during the plasma etching process. The soft organic materials in the litho stacks can bend over and lead to mask flop over when the AR is high. This flop over partially shadows the trench and forms distorted dielectric lines. The dielectrics line itself can also flop over at high aspect ratios, which is most likely due to a combination of high AR and low material strength. In addition, wet treatment post plasma patterning can cause significant flop over due to capillary forces. One of the possible ways to avoid pattern flop over, is to improve the mechanical properties of the mask and dielectric materials. With our research efforts, we hope we can understand and solve this challenge in time to move closer toward the limit of Moore's law.

## 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 AuxPd1-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. Kopczyk, 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. Fournee,* 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 (00001) 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. Beurgler,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 **INVITED**

CO oxidation on Ru, Pd, Rh, and Pt surfaces has been investigated between $10^{-8}$ – 10 Torr and for a variety of temperatures and $O_2$/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 changeling 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. Rossmeisl, 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 alloy[1] has recently been suggested as a promising catalyst for the water-gas shift (WGS) reaction, CO + $H_2O \rightarrow H_2 + CO_2$. 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. Nørskov, 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 $H_2$ 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 microstucture 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 -AlCH$_3$ species. The -AlCH$_3$ species then react preferentially with the hydroxyl end of ethanolamine (EA) to form a surface terminated with -NH$_2$ 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 ºC. 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 ºC to 8 Å per ABC cycle at 150 ºC. 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'Patchen, 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 $(Al\text{-}O\text{-}CH_2CH_2\text{-}O)_n$. These $(Al\text{-}O\text{-}R\text{-}O)_n$ polymer films are known as alucones. The reaction of DEZ with organic diols produces zinc-containing $(Zn\text{-}O\text{-}R\text{-}O)_n$ 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$_2$O$_3$ 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$_2$O$_3$ 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$_2$O for Al$_2$O$_3$ and di-ethyl zinc and H$_2$O 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 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$_3$O$_4$, Co, and Ni in two steps. ALD is first used to deposit Fe$_2$O$_3$,[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.

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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) Al2O3 and ZnO ALD processes onto 3D polyvinyl alcohol electrospun fiber matrix templates to form Al2O3, ZnO and Al2O3/ZnO/Al2O3 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 Al2O3 layers in the Al2O3/ZnO/Al2O3 coaxial structures can react with each other, due to the solid-state reaction and diffusion process between ZnO/Al2O3 (Kirkendall effect), to form pairs of coaxial ZnAl2O4 hollow nanotubes separated by a nanoscale gap. Moreover, by controlling the thickness of the individual Al2O3 and ZnO layers and the ZnO/Al2O3 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.

## 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 (< 2nm) 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 bee used to profile across the interface and in the best cases a depth resolution of < 20 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 Kα 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 surface[1-3] 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 BESSY[7] and SPring8[8] 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]

Work supported by the U.S. Dept. of Energy under Contract No. DE-AC03-76SF00098, and by the Helmholtz Association and the Humboldt Foundation.

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[9] L. Plucinski, J. Minár, et al., Phys. Rev. B, submitted.

[10] A. Winkelman and C.S. Fadley, to be published.

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 <3μm 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 SrHfO$_3$ Thin Films on Si(100)**, ***M. Sawkar-Mathur***, University of California, Los Angeles, *C. Marchiori, J. Fompeyrine,* 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, SrHfO$_3$, 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 SrHfO$_3$ films. Nearly epitaxial growth of SrHfO$_3$ on Si was observed with good crystalline quality and some misalignment of grains. From the in-plane diffraction pattern, the SrHfO$_3$ (100) plane was found to be parallel to the Si(110) plane, yielding a 6% lattice mismatch. The d spacing of the SrHfO$_3$ (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 SrHfO$_3$ (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 SrHfO$_3$ (001) plane. Cluster models with a radial distance of 4 Å were constructed using the perovskite crystal structure of SrHfO$_3$ 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 SrHfO$_3$ on Si has the potential to be a crystalline metal oxide for implementation in CMOS devices.

## 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 surface[1-5]. 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 bonds[6]. 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 proximallayer 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**, ***S. Ritz***, 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.

[1] Kasemo, B., Biological Surface Science. Surface Science, Vol. 500 (2002) 656.

[2] Zaech M., Haegglund C., Chakarov D., Kasemo B., Current Opinion in Solid State and Materials Science Vol. 10 (2006) 132.

## Energy Science and Technology Focus Topic
## Room: 203 - Session EN+SE+NS+SS-MoA

## Hydrogen Storage

**Moderator:** J.F. Herbst, General Motors R&D Center, E. Ronnebro, Sandia National Laboratories

2:00pm **EN+SE+NS+SS-MoA1 Hydrogen Storage for Automotive Vehicles: Methods and Materials*, J.F. Herbst***, General Motors R&D Center

Fuel cells operating on hydrogen are a strong potential alternative to internal combustion engines relying on fossil fuels for a variety of reasons. If a hydrogen fuel cell transportation future is to be realized, however, several major hurdles must be overcome, among them a light, compact, robust, and cost-effective system for storing hydrogen on a vehicle. High pressure compressed gas is a viable option, but its implementation on the commercial scale raises serious manufacturing and cost challenges. A similar statement applies to cryogenic liquid storage, for which dormancy is an additional issue. There is justifiable optimism that new materials may offer significant improvement of the prospects for two other options: (1) hybrid approaches combining compressed gas and a high surface area physisorption medium at 77K, and (2) reversible storage near ambient conditions. Progress on the broad materials front as well as recent research at GM R&D will be discussed.

2:20pm **EN+SE+NS+SS-MoA2 Response of Ultra-Thin Palladium Films to Hydrogen Exposure Studied by Low Energy Electron Microscopy and Diffraction*, B. Santos,*** Universidad Autonoma de Madrid, Spain*, J.I. Cerda, J. de la Figuera,* CSIC, Spain*, K.F. McCarty,* Sandia National Laboratories*, J.M. Puerta*, CSIC, Spain

The ability of Palladium to store hydrogen is well known. Nevertheless surface science studies of the exposure of Pd(111) samples to hydrogen have found only a dense hydrogen layer betwen the last palladium-palladium layers, with additional hydrogen going into the bulk as a solid solution.[1,2] On Pd films a few atomic layers thick on a substrate which does not accept substantial quantites of hydrogen such as Ru, it should be possible to saturate completely the Pd film, and thus study the formation of PdH hydride with surface science techniques. In particular, as there is a substantial lattice mismatch betwen Pd and the beta-PdH hydride, the incorporation of H in Pd-intersticial places should induce a significant expansion of the Pd layers. Although H itself is basically invisible to low energy electron diffraction, the change of the Pd-Pd distances should be easily resolvable by LEED.[3] In this work, we present a low energy electron microscopy study of the hydrogren exposure of thin films of Pd on Ru(0001) and W(110). We characterize and study the growth and structure of Pd thin films. LEEM is a useful technique to monitor and control the growth of thin films in real space. Furthermore, a LEEM microscope can be used to acquire selected area diffraction (SAD-LEED) to determine the structure of such film.[4] Our experiments reveals that Pd films 2 to 6 ML thick on Ru(0001) follow the fcc sequence with the Ru in-plane lattice spacing, and present a corresponding expansion in the out-of-plane lattice spacing. Thicker films on Ru(0001) relax to a bulk-like Pd in-plane spacing. Both thick films on Ru(0001) or W(110) show a slight expansion of the last interlayer spacing, in line with reported studies on the surface of bulk Pd. We follow the dosing of atomic H on the Pd films by means of real-time LEED IV curves acquired by LEEM. We have found preliminary indications that room and low temperature exposure produce a significant expansion in the interlayer distance for a 4 ML thick film. But this expansion is smaller that the one expected for a full PdH beta-hydride formation.

[1] G.E. Gdowski, T.E. Felter and R.H. Stulen Surf. Sci. 181, L147, (1987)

[2] Sampyo Hong and Talat S. Rahman Phys. Rev. B 75, 155405 2007

[3] T. E. Felter, Eric C. Sowa, and M. A. Van Hove, Phys. Rev. B 40 num. 2, 891-899, (1989)

[4] J. de la Figuera, et al, Surf. .Sci. 600, L105 (2006)

2:40pm **EN+SE+NS+SS-MoA3 Destabilized Magnesium-based Alloy Thin Films as Model Systems for Hydrogen Storage**, ***D. Mitlin****, J. Haagsma, C. Ophus, C.T. Harrower,* University of Alberta and NRC National Institute for Nanotechnology, Canada*, M. Saoudi, H. Fritzsche*, National Research Council Canada, SIMS, Canadian Neutron Beam Centre, Chalk River Laboratories **INVITED**

The key for achieving 100 °C - range hydrogen sorption is to have favorable thermodynamics, i.e. a hydrogen binding energy near 30 kJ/mol. Metallic magnesium possesses sufficient gravimetric and volumetric sorption capacity, but has unfavorable thermodynamics (-77 kJ/mol α-MgH2 formation energy) and poor kinetics. In this presentation I will discuss our general methodology for tuning the hydrogen sorption thermodynamics of magnesium, through alloy design. We use a thin films approach to create a range of destabilized magnesium-based alloys and of accompanying catalytic layers. Thin films make for ideal "model" systems that may be used for accurately and rapidly screening a variety of matrix and catalyst formulations. Because of the small diffusion distances, films also allow for better separation of system thermodynamics from the kinetics. The synthesized films were tested volumetrically through multiple adsorption-desorption cycles. The microstructures were characterized by neutron reflectometry and x-ray diffraction. We show that alloying magnesium with light elements that have weak hydrogen interaction, such as aluminum, is a very effective method for lowering the sorption temperature to near ambient. At certain compositions, the addition of aluminum promotes the high-pressure γ-MgH2 phase at the expense of the equilibrium α-MgH2. At other compositions, the sorbed microstructure is a composite of α-MgH2 intermixed with α-AlH3. We also demonstrate that there is critical temperature above which the palladium catalyst caps are not stable, reacting with the underlying material and losing their efficacy. Additionally, there will be a discussion of the processing and sorption kinetics of MgH2 - metal catalyst - carbon nanotube (CNT) powder composites, and of direct TEM characterization of milled MgH2.

### 3:20pm **EN+SE+NS+SS-MoA5 Thermodynamics and Kinetics of Hydrogen Storage in Metallic Nanoparticles Studied by Surface Plasmon Resonance Spectroscopy and Quartz Crystal Microbalance Techniques**

*C. Langhammer, **I. Zoric,*** Chalmers University of Technology, Sweden, *S.T. Kelly, B.M. Clemens,* Stanford University, *B. Kasemo*, Chalmers University of Technology, Sweden

Nanosized metallic particles may have advantageous hydrogen storage properties compared to the corresponding bulk material both in terms of sorption/desorption kinetics and in terms of storage capacity. In order to understand the physical principles behind the influence of nanosizing on hydrogen uptake/release properties, we have developed a novel localized surface plasmon resonance (LSPR) based optical hydrogen sensing scheme for nanoparticle storage systems. As model experiments we carried out measurements of the phase diagram and thermodynamic properties for supported Pd nanodisks, ranging in size from 30 nm to 300 nm. By monitoring the shift of the LSPR extinction peak upon hydrogen uptake/release as a function of hydrogen pressure, at different temperatures, we have mapped out a series of pressure-concentration (p-C) isotherm for a range of particle sizes. These optical studies are complemented by gravimetric studies using a quartz crystal microbalance (QCM). In the latter case the corresponding p-C isotherms were obtained by monitoring the frequency shifts when the Pd nanodisks were prepared on the QCM electrode and exposed to hydrogen environment at different temperatures. We have used Van't Hoff plots (log of the isotherm plateau pressure, in the two-phase region, versus inverse plateau temperature), to obtain the enthalpy and entropy for hydride formation in Pd nanodisks of different sizes. Furthermore, we have used Sievert's plots in the low hydrogen concentration limit (α-phase) to extract enthalpies and entropies of hydrogen dissolution. An excellent agreement was obtained for the corresponding thermodynamic variables obtained from LSPR sensing data and QCM data. Similarities and differences to the corresponding thermodynamic variables for bulk systems are discussed. In addition, we have carried out corresponding measurements with Mg nanoparticles "capped" with few nanometers of Pd to facilitate H2 dissociation. The "capping" with a Pd layer circumvents the bottleneck associated with low dissociative sticking of hydrogen on Mg. Double plateau isotherms were obtained indicating initial onset of the mixed phase formation at low hydrogen pressure in Mg nanoparticle followed by a corresponding two phase onset in the Pd cap at higher pressure, characteristic for Pd nanoparticles at a given temperature. In addition, we also present the QCM and LSPR based studies of hydrogen uptake/release kinetics at different temperatures.

### 4:00pm **EN+SE+NS+SS-MoA7 Atomistic Mechanisms of Reversible Hydrogen Storage in Complex Metal Hydrides**

***P. Sutter***, Brookhaven National Laboratory **INVITED**

The storage of hydrogen in a lightweight, high-capacity medium with fast charge/discharge kinetics has been recognized as one of the primary challenges in achieving the transition to a hydrogen-based economy. Hydrogen-rich compounds, such as complex metal hydrides, offer potentially high storage capacities but the solid-state hydrogen storage reactions in these materials generally proceed slowly and in many instances are not reversible, i.e., re-hydrogenation of the depleted products cannot be realized by controlling temperature and hydrogen pressure alone. The use of doping to achieve reversibility and fast reaction kinetics has been demonstrated successfully for a particular complex metal hydride, sodium alanate (NaAlH$_4$). Here we discuss our recent efforts on identifying the atomic-scale effects of such doping by microscopy and spectroscopy experiments on well-defined model systems (e.g., single crystal surfaces), closely linked to ab-initio theory and simulations. A comprehensive understanding of important microscopic reaction mechanisms allows deriving general guidelines for the use of dopants or catalysts to accelerate hydrogen storage reactions in alanates, and possibly in a broader class of solid-state storage materials.

### 4:40pm **EN+SE+NS+SS-MoA9 Microwave Irradiation for the Reversible Desorption of Hydrogen from Sodium Aluminum Hydride**

***T.A. Dobbins***, Louisiana Tech University and Grambling State University, *R. Krishnan*, Louisiana Tech University

Materials such as complex metal hydrides and hydrogen adsorbents have been the primary focus of the on-board hydrogen storage research program. Complex metal hydrides offer great potential in making it into the transportation industry due their reliable on-board reversibility. These materials can perform very well even after multiple dehydrogenation-hydrogenation cycles. Conventional heating mechanisms have been used to desorb hydrogen from complex metal hydrides. However, conventional heating processes involve high energy penalties (because the energy invested to heat the complex metal hydride is equal to or greater than the energy generated by a fuel cell using the desorbed hydrogen). This research is aimed at establishing the use of microwave irradiation to desorb hydrogen from sodium aluminum hydride (NaAlH4). Microwave heating is known to be more energy efficient than conventional heating. However, microwave fields are also known to drive order to disorder reactions in the hydrides, thus resulting in amorphous desorption products. This work reports a method to use microwave irradiation to desorb hydrogen from NaAlH4 via the reversible desorption pathway. This is the first report of using microwaves to drive a dehydrogenation reaction with the same pathway as driven by conventional heating processes. The method established in this research makes use of the energy efficiency of microwave irradiation and can be extended to other hydride systems for future research.

Funding for this project was provided by the Department of Energy, Office of Basic Energy Sciences (Contract No.: DE-FG02-05ER46246).

### 5:00pm **EN+SE+NS+SS-MoA10 Alane Formation on Al(100) and Ti-doped Al(100)**

***I.S. Chopra**, J.-F. Veyan, Y.J. Chabal,* University of Texas at Dallas, *S. Chaudhuri*, Washington State University

Complex metal hydrides, such as NaAlH$_4$, are candidates for hydrogen storage as they can reversibly release and recapture hydrogen. Alane Clusters (Al$_x$H$_y$) are believed to be the mass transport intermediate in the hydrogen storage reactions involved in hydrogen uptake and release. Understanding the surface chemistry behind the formation and evolution of alane clusters is therefore important to lower the temperatures needed for these processes. Since doping metallic Al is critical for H$_2$ dissociation, we have undertaken a comprehensive study of H interaction with Al(100) and Ti-doped Al(100) surfaces to better understand the atomic scale mechanisms underlying this reversible hydrogen storage behavior. The results have been compared with similar study performed earlier on the Al(111) and Ti doped Al(111) surface. In-situ infrared absorption spectroscopy had previously shown[1] that the nature of alanes (size, bonding configuration) formed on Al(111) depends on both H exposure and sample temperature. At low temperatures (~90K), small alanes such as AlH$_3$ and Al$_2$H$_6$ are predominant. At higher temperatures (~ 250K), larger alanes are formed. The study of alane formation on the Al(100) surface as a function of H exposures and substrate temperatures make it possible to explore the dependence of the alane formation on the crystal orientation. The effect of Ti doping is also explored as a function of both Ti concentration and H$_2$ pressures. Our first-principles calculations indicate that Ti atoms should occupy hollow sites of the (100) unit cell. We are therefore using LEED to test whether this site is indeed the most favorable and IR spectroscopy to explore whether Ti in that site does dissociate H$_2$. On Al(111), no dissociation was observed for H$_2$ pressure up to 10$^{-6}$ Torr. We are therefore exploring dissociation up to 10$^{-4}$ Torr on Al(100). Finally, we are using TPD to probe the nature of desorbed species from both Al(100) and Ti – doped Al(100) surfaces.

[1] Santanu Chaudhuri, Sylvie Rangan, Jean-Francois Veyan, James T. Muckerman,Yves J. Chabal, J.Am. Chem. Soc. (submitted).

### 5:20pm **EN+SE+NS+SS-MoA11 Infrared Spectroscopy Studies of Hydrogen Interaction in Metal Organic Frameworks**

***N. Nijem**, J.-F. Veyan*, University of Texas at Dallas, *J. Li*, Rutgers University, *Y.J. Chabal*, University of Texas at Dallas

Hydrogen storage is one of the most challenging problems in hydrogen-based energy technology. One of the goals of hydrogen storage is the ability to store a high volumetric density of hydrogen at room temperature. As a result, studies exploring hydrogen interaction in storage materials are important to facilitate further development of materials. Metal-organic Frameworks are promising candidates for hydrogen storage because their high surface area and porosity facilitate high hydrogen physisorption on specific sites of the structures. This work explores the incorporation of hydrogen into the structure using infrared (IR) absorption spectroscopy. IR spectroscopy can distinguish possible H$_2$ binding sites based on the perturbation of the internal H$_2$ stretch mode. The measurements are performed at room temperature on three different types of MOF structures, two of which have the general formula [M(bdc)(ted)$_{0.5}$]-2DMF-0.2H$_2$O, differing in the metal core M (Ni and Zn). These two compounds are isostructural and crystallize in the tetragonal phase (space group P4/ncc), they construct a 3D porous structures with relatively large pore size (~7-8Å, pore volume (~0.63-0.84 cc/g) and BET surface area (~1500-1900 m$^2$/g). Another type of MOF is the [Ni$_3$(HCOO)$_6$]-DMF structure which crystallizes in space group P21/c and features a 1D open channels with smaller pore diameters (~5-6 Å). Preliminary results show perturbation of the H$_2$ gas vibrational modes leading to a ~30 cm$^{-1}$ shift of the ortho- and para- peaks of the unperturbed H$_2$. This perturbation is due to the interaction of the hydrogen with the MOF and can be seen as evidence of the hydrogen adsorbed onto specific sites of the MOF. Although the data are taken for high pressure H$_2$ gas at room temperature, the shift is consistent with previous observation of Bordiga et al.[1] performed at very low pressures and temperatures. The intensities of the perturbed ortho- and para- H$_2$ peaks have a linear dependence with pressure, indicating that the perturbation of the $H_2$ with the MOF lattice is dominant, i.e. $H_2$-$H_2$ interactions are much less important than in the pure $H_2$ gas.

[1] S. Bordiga, J. G. Vitillo, G. Ricchiardi, et al., Interaction of hydrogen with MOF-5 Journal of Physical Chemistry B 109, 18237 (2005).

## 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 bandgaap 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.

[1] J. 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).

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

[3] S. 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's[1] 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 mm$^2$ to 4000 mm$^2$ 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 cm$^2$ /Vs).

[1] C. 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.

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

[2] G. 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

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

[2] G. 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.

## IPF 2008 Frontiers in Imaging: from Cosmos to Nano
## Room: 312 - Session IPF+NC-MoA

### Materials Imaging with Subatomic Resolution

**Moderator:** R. Ludeke, IBM (Retired), J. Murday, University of Southern California

2:00pm **IPF+NC-MoA1 Spatially Resolved Vibrational Imaging with Sub-Nanometer Resolution**, ***W. Ho***, University of California, Irvine **INVITED**

Vibrational spectroscopy has proven to be a powerful technique for chemical analysis, and its capability has been improved steadily over the years. At the limit of sensitivity is the detection of the vibration of a single bond and the imaging of such a signal would provide unprecedented spatial resolution in chemical visualization. In addition to revealing the chemical constituents at the atomic level, vibrational imaging at the sub-nanometer scale also can provide dynamical information such as charge and energy transfer, electron-vibrational coupling, and light-matter interaction. With the initial demonstration of inelastic electron tunneling spectroscopy and microscopy with a scanning tunneling microscope (STM), it is now possible to investigate with atomic scale resolution a wide range of inelastic phenomena that involve vibrational excitation. The scanning capability of the STM enables vibrational imaging of the interior of single molecules, their interactions with the environment, the coupling of electrons to vibrations in electron transport, and optical phenomena with atomic scale spatial resolution.

2:40pm **IPF+NC-MoA3 Attosecond Nanoplasmonic-Field Microscope**, ***M.I. Stockman***, Georgia State University, *U. Kleineberg*, Ludwig-Maximilians University, Germany, *M. Kling*, *F. Krausz*, Max Plank Institute for Quantum Optics, Germany **INVITED**

Nanoplasmonics deals with collective electronic dynamics, which arises due to elementary excitations called surface plasmons. Because of the very broad bandwidth, the surface plasmons undergo ultrafast dynamics unfolding on time scales as short as a few hundred attoseconds. So far, the ultrafast spatiotemporal dynamics on the nanoscale has been hidden from direct access in the real space and time. We propose an approach that will, for the first time, provide direct, non-invasive access to the nanoplasmonic dynamics with nanometer-scale spatial resolution and on the order of a few hundred attoseconds temporal resolution. This method combines photoelectron emission microscopy and attosecond streaking metrology. It offers a valuable new way of probing ultrafast nanolocalized fields in nanoplasmonic systems. This approach will be interesting both from a fundamental point of view and in the light of the existing and potential applications of nanoplasmonics.

4:00pm **IPF+NC-MoA7 Atomic Motion Observed with sub-Angstrom Resolution in the Electron Microscope**, ***P.E. Batson***, IBM T.J. Watson Research Center **INVITED**

The recent successful introduction of aberration correction optics into the electron microscope has produced an instrument that can routinely image the positions of single atoms and structure of small groups of atoms. In fact, the signal from a single atom is strong enough to obtain good quality images in a few tens of milli-seconds, allowing the taking of sequences of images to follow atomic processes. In the microscope, atomic level objects are vigorously excited by the electron beam, and this energy deposition is observed to speed up normal processes – island coalescence, structural changes, and nucleation of growth -- so that they are observable in relatively short times. In many cases, imaging in bulk specimens shows similar atomic level behavior. Thus stress relaxation and atomic redistribution within bulk structures may be observable in the presence of the electron beam, and so may be quantified if the electron beam interaction can be well understood. The combination of Electron Energy Loss Spectroscopy with atomic resolution imaging promises to obtain local electronic structure within the bulk, but changes in the bulk structure caused by energy deposition will complicate interpretation. This presentation will discuss these observations and suggest what types of mechanisms may contribute to the observed behavior.

4:40pm **IPF+NC-MoA9 Force Microscopy with Subatomic Resolution,** ***F.J. Giessibl***, University of Regensburg, Germany **INVITED**

A theoretical analysis of the factors that determine the spatial resolution of the force microscope led to the conclusion that optimal results are expected to occur when the oscillation amplitude of the cantilever in dynamic atomic force microscopy (AFM) has a magnitude similar to the range of the forces at play. When the cantilever is to oscillate with small amplitudes in a stable fashion under the influence of the field of the chemical bonding forces present between tip and sample, cantilevers with a stiffness of roughly 1kN/m instead of the commonly used 40 N/m are required.[1] Soon after these findings, experimental force microscopy data was published that shows "subatomic" resolution, that is the imaging of features within single atoms.[2] While these findings were debated, a direct comparison of scanning tunneling microscopy and AFM data showed that when probing a tungsten tip with a graphite surface (a "light-atom probe"), subatomic orbital structures with a spatial resolution of less than one Angstrom can be obtained in the force map, while a map of the tunneling current only shows the known atomic resolution.[3] Optimized subatomic contrast is obtained when recording the higher harmonics of the cantilever motion.[3] The idea of the light atom probe was carried further in a collaboration with the IBM Low Temperature STM group in Almaden, San Jose where an adsorbed CO molecule was used to probe the tip atom. It requires quite a large force to move a CO molecule laterally[4] and this molecule is an excellent probe for the orbital structure of the front atom of the metal tip. Ideally, one wishes to create a probe with a perfectly perpendicularly oriented CO molecule at the very end of the tip. First steps towards that goal will be discussed. We also address the question why "traditional" dynamic AFM has apparently not yet demonstrated subatomic resolution.

[1] F.J. Giessibl, H. Bielefeldt, S. Hembacher and J. Mannhart, Appl. Surf. Sci. 140, 352 (1999); F.J. Giessibl, Rev. Mod. Phys. 75, 949 (2003).

[2] F.J. Giessibl, H. Bielefeldt, S. Hembacher, J. Mannhart, Science 289, 422 (2000).

[3] S. Hembacher, F. J. Giessibl, J. Mannhart, Science 305, 380 (2004).

[4] M. Ternes, C. P. Lutz, C.F. Hirjibehedin, F.J. Giessibl, A. J. Heinrich, Science 319, 1066 (2008).

5:20pm **IPF+NC-MoA11 Cryolectron Microscopy of Biological Macromolecules on Its Way Toward Near Atomic Resolution and Multiple Conformations, *U. Luecken***, FEI Company, The Netherlands, *H. Zhou*, University of California, Los Angeles, *H. Stark*, Max Planck Institute of Biophysical Chemistry, Germany **INVITED**

I will report on the latest results just shown at the Gordon conference on Three dimensional Electron Microscopy and found teo of the world leading scientists in macromollecular complex imaging and Virus research.

## 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 silsesquioxane 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.

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

[2] H. 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 $SiO_2$ (100 nm)/$Si_3N_4$ (20 nm)/TiN (30 nm)/$Si_3N_4$ (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 $CHF_3$+$O_2$ and $CH_4$ steps to remove $SiO_2$ and $Si_3N_4$/TiN/$Si_3N_4$, 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 $Si_3N_4$ (5 nm)/a-Si (20 nm)/$SiO_2$ (100 nm) films on a bulk Si substrate. PMMA (200 nm thickness) line patterns fabricated by e-beam lithography were transferred to the $Si_3N_4$, a-Si and $SiO_2$ layers through a multi-step RIE process, which generated ~50 nm width and ~60 nm depth trench structures. Then, a selective isotropic etching of $SiO_2$ 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 $TiO_2$ 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 ~$10^5$ 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 attonewton 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 $10^3$ 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.[2] 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-8[2] 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.

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

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

5:00pm **MN+NC-MoA10 $XeF_2$ 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

$XeF_2$ 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 stoichoimetric oxides. Understanding the etching mechanisms is crucial to achieve highly selective etching. We have studied and compared the $XeF_2$ 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 $XeF_2$ introduction. The sample temperature prior and during $XeF_2$ 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 $SiO_2$/Si, and grazing angle reflection to probe $MoO_3$/Mo, and surface and subsurface species are detected/identified during and after etch reactions. $XeF_2$ induces a strongly exothermal reaction with both Si and Mo, producing gaseous $SiF_4$ (1030 $cm^{-1}$)and $MoF_6$ (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.

## Plasma Science and Technology
## Room: 304 - Session PS-MoA

## Invited Highlights on Plasma-Surface Interactions - Honoring the Distinguished Career of Herbert H. Sawin
**Moderator:** J.P. Chang, University of California, Los Angeles

2:00pm **PS-MoA1 Plasma Etching - The Early Days*, J.W. Coburn***, University of California at Berkeley

Remarkable progress has been made in the implementation and understanding of the pattern transfer capabilities of plasma etching in the 30 or so years this technique has been used in microelectronics manufacturing. Where did it all begin? One perspective of some of the early highlights introduced in the mid-1970s will be presented. The importance of studies supporting physical sputtering (both sputter-etching and sputter-deposition) using Ar glow discharges will be emphasized. A select few pioneering advances in processing chemistries will also be described.

2:20pm **PS-MoA2 Following Moore's Law – How Many Knobs are Enough?*, R.A. Gottscho*, *K. Smekalin***, Lam Research **INVITED**

With the introduction of 3x technology, more new materials are introduced into semiconductor devices and their manufacture. Yet, the basic etch challenges do not change qualitatively: selectivity, profile, uniformity, damage, line edge roughness and more. Quantitatively, of course, virtually everything changes: with each shrink, the difficulty in meeting the tolerances increases along with cost. The tightening of tolerances on the die, the wafer, and the system places un-precedented demands on system and sub-system variability reduction – active and passive. For repeatable, high yield, high output manufacturing, minimizing variability is essential. Yet the requirements to shrink stimulate increased demands for more control "knobs." Some knobs are provided to compensate for asymmetric limitations in design or inherent non-uniformities. Other knobs are provided to expand process flexibility in the hope of facilitating recipe optimization. The irony is that more control knobs means increased variance in the control parameter vector leading directly to more difficulty in matching chambers and narrower process windows, leading to more manufacturing excursions and downtime. More control knobs also means more recipe complexity. Despite impressive advances in simulation capability, plasma process development remains an empirical endeavor. With the most recent advances in etch production equipment, the number of recipes that have a measurable impact on the wafer are already more than 1 trillion. Can any production recipe be said to be truly optimal? Do more control variables help or hinder our ability to meet next-generation technology challenges? And do they save cost or add cost?

3:00pm **PS-MoA4 Real Time and 3D Characterization Techniques to Control Plasma Etch Processeses at the Nanometer Scale*, O. Joubert***, CEA/LETI-Minatec, France

As the industry approaches the ability to create microcircuit structures on the order of 20 nm, this technology faces fresh challenges. To make progress, we need to go back to the basic science of how plasmas interact with surfaces. Several trends are at work: First, circuit patterns need to be accurate to within 1 nm and below, within a single wafer and across several wafers. Second, plasma etching is becoming an integral part of pattern generation (using lateral erosion of the lithographic photoresist to improve resolution, for example). Third, aspect ratios of the final structures (that is, the ratio of length to width) are increasing dramatically. Finally, the number of potential new material candidates and their possible combinations in future structures is exploding. In this context, understanding the fundamentals of the etch mechanisms and their correlations to key process parameters is crucial. Each etch step must be characterized not only by etch rate and uniformity, but also by more fundamental properties such as the composition, thickness, and line-edge roughness of the sidewall layers of the structure, the chemical nature of etch by-products deposited on the chamber walls (which affects process stability and reproducibility), the thickness of the etch-front mixing layer (correlated to etch rate and selectivities between layers), and the impact of aspect ratio–dependent etching phenomena. In this talk, we will describe in details the latest development in scatterometry that can be used to monitor in real time resist trimming processes or more complex processes. We will also discuss the latest results obtained using the 3D AFM technique to characterize the transfer of photoresist line edge roughness in complex stacks. Finally we will also discus the importance of monitoring passivation layers formed on the feature sidewalls as well as the coatings formed on chamber walls during plasma processes since both impact directly the critical dimension of patterned structures.

3:20pm **PS-MoA5 Three Dimensional Modeling of Surface Profile Evolution During Plasma Etching (Plasma Prize Lecture)*, H.H. Sawin****, Massachusetts Institute of Technology

We have developed a profile simulator capable of modeling both feature scale evolution as well as roughening within the feature during plasma etching. As roughening is inherently a three dimensional phenomenon, we chose to extend our 2.5D Monte Carlo simulation with cellular surface position and composition representation to a full 3D simulation. The surface interaction is computed based on a local polynomial fitting of the surface cells and computing the surface kinetics based upon the particle interaction with this curved surface. An algorithm for addition and removal of cells was developed based upon a balance between adding cells which retain a smooth surface and the addition of cells which advance the surface in the direction of the local surface normal. The simulation was tested against a broad range of conditions and shown to satisfactorily model feature scale profile evolution. To model the surface kinetics, we used a moving mixed surface layer description in which the surface kinetics are based upon the composition in the cell(s) upon which the particle strikes as well and the incident. The kinetics included incident angle dependence with respect to the polynomial's normal, the energy dependence of ion bombardment, and the etching yield dependence on surface curvature. Ion scattering with dispersion about the specular scattering angle of ions as well as dispersion of scattered neutrals and disperse emission of reaction products. Redeposition of reaction products was included as well. With this model, we have successfully simulated the roughening of Si surfaces under Ar ion bombardment demonstrating the creation of surface striations oriented transverse to the direction of ion bombardment at low off-normal angles, smooth surfaces at intermediate off-normal angles, and striations parallel with the ion bombardment at higher incident angles. We have also simulated the transition from transverse to parallel roughening which occurs with increased etching time. We have also successfully modeled oxide and low-K dielectric etching using surface kinetics developed for oxide etching with fluorocarbon discharges.

4:00pm **PS-MoA7 Will Recombination Reaction Probabilities at Plasma Chamber Walls Ever Be Non-Adjustable Parameters?*, V.M. Donnelly***, University of Houston

Reactions of neutral species on surfaces immersed in plasmas have been recognized for many years to be an important class of processes that plays a major role in determining the make-up of species in the plasma. The association of radicals on the surfaces of chamber walls and substrates represents a sink for radicals and a source of larger product species. Chemistry-rich models have been developed in recent years for plasmas such as those used to etch silicon and dielectric materials. Heterogeneous reactions are an essential part of these models. With the exception of a few atom recombination reactions, the reaction probabilities for these processes are completely unknown; hence they are usually treated as adjustable parameters, or are guessed at and left constant. Experimental measurements of these reactions are usually carried out in one of two ways, neither is ideal. First, in-situ measurements can made in the plasma. This approach has the advantage of studying the surface that exists during plasma operation - one that is often coated with amorphous deposits of sputtered or etched substrate and reactor materials, and receives high fluxes of neutrals, ions, electrons and photons. This complexity makes it difficult to isolate individual reactions. Consequently, a second approach has been practiced in which the complex plasma environment can be avoided by studying reactions in high vacuum with selected molecular beam impingement. While this approach can provide accurate measurements of reaction probabilities, product identification and surface characterization, it can also

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* 2008 Plasma Prize Winner

lead to misleading predictions when extended to real plasma conditions. This talk will briefly review a few selected studies that highlight the complexity and lack of consensus in this field, and offer prospects for system-non-specific rate parameters for this class of heterogeneous reactions.

4:20pm **PS-MoA8 Ion-Surface Interactions Beyond Etching*, K.P. Giapis***, California Institute of Technology

Plasma etching has been conceptually distinguished into physical and chemical etching, in reference to the way material is removed from the surface under ion bombardment. There are other ion-surface interactions at play, which have received little attention although they may substantially alter the outcome of the etching process—especially when patterning wafers. We will present evidence from ion beam experiments for the following mechanisms: 1) Eley-Rideal (abstraction) reactions, 2) Electronic excitation as a result of inelastic collisions, 3) Pre-dissociation of molecular ions before collision with the surface, and 4) Coulomb explosion of adsorbed electronegative atoms. The importance of these processes in plasma etching will be discussed.

4:40pm **PS-MoA9 Can Plasma Modeling Be a Predictive Tool in Process Development?: Etching of Very High Aspect Ratio Features and Gate Stacks****, *M. Wang, Y. Yang, J. Shoeb,* ***M.J. Kushner***, Iowa State University

The use of modeling in the development of plasma tools has achieved a significant degree of success. Optimizing the uniformity and energies of reactant fluxes with results of modeling prior to prototyping by varying, for example, the aspect ratio of the reactor or frequency of excitation is now accepted practice. The assist of modeling to develop plasma processes has provided a less clear return on investment. This is due, in part, to the complexity of the reaction mechanism and the lack of fundamental data. The rate of technology development will likely outstrip our ability to generate the required fundamental data, at least in the near term. As such, what are the realistic expectations for modeling to provide high value to the development of plasma processes? In this talk, the general status and the potential success of plasma modeling in the development of processes will be discussed with results from two case studies using reactor and feature scale modeling platforms. In the first, sporadically occurring twisting of via-like features in extremely high aspect ratio etching has been attributed to the stochastic nature of fluxes entering the feature as the size of the opening shrinks. This is an effect exacerbated by charging. Here the reaction mechanism, fluorocarbon plasma etching of Si and $SiO_2$, is relatively well known. So modeling has assisted in developing a dc-augmented strategy for the capacitively coupled tools that addresses the contribution of charging to twisting. In the second, high-k dielectric $HfO_2$ gate stack etching, the reaction mechanism is at best poorly known. Here, the contribution of modeling has been to refine that reaction mechanism based on the existing but fragmentary database and so narrow the now broad range of operating conditions that might be considered in process development.

*Work supported by the Semiconductor Research Corp., Micron Inc., Applied Materials Inc. and Tokyo Electron Ltd.

5:00pm **PS-MoA10 Predictive Etch Profile under Competition Among Deposition, Etching, and Charging on Dielectrics in a Low Temperature Plasma*, T. Makabe***, Keio University, Japan

A dielectric surface exposed to plasma irradiation keeps competitive, physical and chemical processes among etching, deposition, and charging on the local pattern.[1] Top down plasma nano-etching is a technology assisted by a directional and energetic positive ion onto a surface saturated by adsorbed chemical molecules. The ion flux to the wafer has a magnitude of $10^{15}cm^{-2}s^{-1}$. It means that the ion incident on the surface transfers the kinetic energy to the lattice with a relaxation time shorter than the surface collision interval. We have no way to protect the surface from the charging damage, particularly on the dielectric, in a periodically steady state radio frequency (rf) plasma, which always forms the positive ion sheath in front of the biased wafer to be etched. We have demonstrated a technique to inject negative charges having a relatively high energy in a synchronized mode between an rf plasma source with on/off period and a LF bias pulse in order to develop a charging free plasma etching. It is realized by an artificial formation of a double layer close to the wafer.[2,3] The synchronized pulsed operation will enable us to develop a charging free plasma etching. The time constant of local charging, caused by the great difference in the velocity distribution between ions and electrons incident on a topographical surface, is approximately two orders of magnitude shorter than the time for the effective monolayer etching in $SiO_2$. This difference enables us to estimate the etching profile by the two-step evaluation, i.e., surface charging followed by etching. Even in a controlled wafer exposed to a plasma etching, the surface is the competitive processes between etching and deposition, where two-layer model will be efficient in order to predict the feature profile evolution by using Level set method[3]. Predictive images are shown and discussed for the feature profile evolution of dielectric.

[1] T. Makabe and Z. Petrovic, "Plasma Electronics: Applications in Microelectronic Device Fabrication", Taylor & Francis (2006).

[2] T. Ohmori, T. Goto, T. Kitajima, and T. Makabe, Appl. Phys. Lett. 83, 4637-9 (2003); T. Ohmori and T. Makabe, Appl. Surf. Sci. 254, 3696-3709 (2008).

[3] T. Shimada, T. Yagisawa, and T. Makabe, Japan J. Appl. Phys. 45, L132-4 (2006); Ibid. 45, 8876-82 (2006); T. Makabe, T. Shimada, and T. Yagisawa, Comp. Phys. Commun. 177, 64-7 (2007).

5:20pm **PS-MoA11 Silicon Processing Technologies in Adjacent Spaces: Applications Beyond Information Technology*, T. Dalton***, IBM

Over the course of the last fifty years, the microelectronics industry has made tremendous strides in the development and manufacturing of ever more complex integrated circuits (IC). These circuits have typically been applied to the information technology (IT) industry and have driven improvements in the computational power per dollar of many orders of magnitude. Part of the "toolbox" of skills acquired to produce integrated circuits is the ability to form desired patterns at ever decreasing sizes. The minimum controllable feature size has been reduced by six orders of magnitude (from millimeters to nanometers) during the last fifty years. With feature sizes rapidly approaching 10nm, the conventional silicon IC industry is nearing a threshold with the end of conventional silicon scaling approaching. Research today focuses on new device structure to replace the CMOSFET as the engine of the IT industry. Another very active research area is the concept of taking the skill-set acquired from IC research, development, and manufacturing, and to apply those skills into new area – "adjacent spaces" where the ability to machine patterns at very small sizes may open up new areas of research and development, and to form the basis for future industries.

## 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-$Ga_2O_3$ Nanoribbons*, V.M. Bermudez,*** *S.M. Prokes*, Naval Research Laboratory

β-$Ga_2O_3$ 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 series[1-3] of computational and experimental studies of β-$Ga_2O_3$ 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 $H_2O$ and $CH_3OH$ is still somewhat more favorable than chemisorption, but formation of a bridging formate species is favored for $HCO_2H$. 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-$Ga_2O_3$.

[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 $TiO_2$(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 $CH_2O$ with perfect and defective $TiO_2$(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 $TiO_2$(110) surface to $CH_2O$ at 100 K leads to the formation of physisorbed $CH_2O$ and paraformaldehyde. The latter decomposes to $CH_2O$ that desorbs at about 270 K. On the defective $TiO_2(110)$ surface $CH_2O$ adsorbs more strongly on oxygen vacancy sites ultimately forming a diolate (-$OCH_2CH_2O$-) 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 $O_2$ Dissociation at Oxygen Vacancies of $TiO_2(110)$**, *Y. Du, Z. Dohnalek, **I. Lyubinetsky***, Pacific Northwest National Laboratory

The interaction of molecular oxygen with $TiO_2$–based materials affects many chemical and photochemical processes. We will present our recent discoveries in studying $O_2$ interaction with reduced $TiO_2(110)$ surface by scanning tunneling microscopy at 300K. By tracking the same surface area before and after $O_2$ exposure, we confirm the known $O_2$ dissociation channel occuring 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 $O_2$ Dissociation on Ti rows of Reduced $TiO_2(110)$**, ***Y. Du**, Z. Zhang, Z. Dohnalek, I. Lyubinetsky*, Pacific Northwest National Laboratory

The interaction of molecular oxygen with $TiO_2$ plays a critical role in catalytic activity of $TiO_2$-based materials. It is generally agreed that reactivity of $TiO_2$, 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 $O_2$ and reveal another $O_2$ dissociation channel, where an oxygen molecule dissociates on rows of five-fold coordinated Ti atoms to form an oxgyen adatom pair with two lattice constants spacing. We believe the discovery of the additional $O_2$ dissociation channel could have a considerable impact on the $TiO_2$ 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 $TiO_2$: 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 $TiO_2(110)$ 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 $V^{5+}$ while $V^{4+}$ 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 $V^{5+}$ 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 $V^{5+}$ and $Ti^{4+}$. It is also found that the activation energy of the lower temperature channel is stable on the submonolayer film, independent of reduction and reoxidaton, 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 $TiO_2$ 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 $TiO_2(110)$ 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 $TiO_2$ 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 $TiO_2(110)$: Oxygen Adsorption and Reactions with Oxygen Vacancies**, *G.A. Kimmel, **N.G. Petrik***, Pacific Northwest National Laboratory

The interaction of oxygen with $TiO_2$ 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 $TiO_2(110)$ is investigated using temperature programmed desorption and electron-stimulated desorption.[1] At low temperatures, two $O_2$ molecules can be chemisorbed in each oxygen vacancy. These molecules do not desorb upon annealing to 700 K. Instead for $200 \text{ K} < T < 400 \text{ K}$, the two $O_2$ convert to another species which has four oxygen atoms, i.e. tetraoxygen, that decomposes at higher temperatures. In contrast when only 1 $O_2$ 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 $TiO_2(110)$, are consistent with the recent prediction that $O_4^{2-}$ 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 $TiO_2(110)$ 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. Rabufetti*, 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 $MeCpPtMe_3$ precursor combined with $O_2$ gas and $O_2$ 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 $O_2$ 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 $g/cm^3$ and an electrical resistivity of 14 μΩ cm, both close to the bulk values of 21.4 $g/cm^3$ and 10.8 μΩ cm. The platinum oxide films had a mass density of 8.9 $g/cm^3$ 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 $MeCpPtMe_3$ 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 $SiO_2$ ALD Using Tris(tert-Pentoxy)Silanol**, ***S.M. George***, *B.B. Burton*, University of Colorado

Rapid $SiO_2$ ALD can deposit very thick, ~100 Å, conformal $SiO_2$ films by exposure of various silanol precursors to surfaces covered with Al-catalysts. Rapid $SiO_2$ ALD with tris(tert-butoxy)silanol (TBS) was reported at temperatures from 200─300°C and deposited $SiO_2$ 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 $SiO_2$ ALD films using liquid tris(tert-pentoxy)silanol (TPS). TPS can deposit even thicker $SiO_2$ films at lower temperatures. The rapid $SiO_2$ 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 $SiO_2$ film. The $SiO_2$ film thicknesses deposited during one silanol exposure are dependent on the temperature, silanol pressure, and silanol exposure time. $SiO_2$ film thicknesses were determined using quartz crystal microbalance and x-ray reflectivity measurements. For TPS exposures of 1 second, the $SiO_2$ ALD growth rate was larger at lower temperatures and larger TPS pressures. $SiO_2$ 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 $SiO_2$ 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 $SiO_2$ ALD mass gains decreased with increasing delay times. This behavior suggested that the longer delay times produced more cross-linking that self-limits the $SiO_2$ deposition. Other experiments showed that higher temperatures produced faster nucleation of the rapid $SiO_2$ 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 $SiO_2$ 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 $TiO_2$ using titanium tetraisopropoxide (TTIP) as the metal precursor and $O_3$, atomic O, and $H_2O$ 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 $TiO_2$. We find that the surface reaction mechanism is very different for $O_3$- and $H_2O$-based ALD. Surface hydroxyl groups are generally the reactive sites for the metal precursors in a $H_2O$-based ALD process. In contrast, we do not detect any hydroxyl groups on the surface after the $O_3$ cycle. Our data shows that the reactive sites for the adsorption of TTIP after $O_3$ 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 carbonated 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 $O_3$ exposure, $CO_2$ and $H_2O$ are formed due to the combustion of isopropoxy ligands and a small fraction of these molecules react with the $TiO_2$ surface producing these surface carbonates. $CO_2$ 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, $CO_2$ from the carbonates was released into the gas phase and was again detected by the IR beam. Using $O_3$ as the oxidizer, relatively contaminant-free $TiO_2$ films were deposited at 150 °C: this is nearly 100 °C lower than the widely-accepted minimum temperature for the TTIP-$H_2O$ 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 $HfO_2$ ALD on GaAs**, ***T. Gougousi***, *J.C. Hackley*, UMBC, *J.D. Demaree*, Army Research Laboratory

The atomic layer deposition of $HfO_2$ thin films is studied on GaAs(100) surfaces. The films are grown using tetrakis(dimethyl)amino hafnium (TDMAH) and $H_2O$ precursors at a deposition temperature of 275°C. Several GaAs starting surfaces are investigated, including native oxide and both HF and $NH_4OH$-treated substrates. Wet chemical etching in either HF or $NH_4OH$ 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 $2.6\times10^{14}$ Hf/cm$^2$/cycle is reached after 10 ALD cycles for the HF-etched GaAs surface while much smoother growth is observed for the native oxide surface (~$2.9\times10^{14}$ Hf/cm$^2$/cycle). The interface of $HfO_2$ films deposited on GaAs surfaces is probed by X-ray photoelectron spectroscopy. Both the HF and $NH_4OH$ treatments passivate the surface and prevent the oxidation of the interface during the deposition of coalesced $HfO_2$ films (> 15 ALD cycles). Deposition of $HfO_2$ 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.

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[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. Shahrjerdi, 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 streching modes are evident at low temperatures for the HTB reaction while Hf-H streching 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 $Co_2(CO)_8$ and $Co(C_5H_5)(CO)_2$ 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 ºC. 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 ºC are not widely available. Previous studies of CVD Co from $Co_2(CO)_8$ show a transition in reaction kinetics at temperatures near 100 - 150 ºC, 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 ºC using $Co_2(CO)_8$ and $H_2$ gases using on-line quadrupole mass spectrometry and Auger electron spectroscopy. Similar experiments using cobalt cyclopentadienyl dicarbonyl and $H_2$ reactants were also performed between 140 and 350 ºC. 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 ºC, with no indication for self-limiting precursor adsorption. The observed continuous film growth with the $Co_2(CO)_8$ 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 Co(cyclopentadienyl), without film growth at less than 300 ºC. 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 spectroscope (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 $SiO_x$ 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).

## Vacuum Technology
## Room: 205 - Session VT-MoA

## Vacuum Cleanliness, Outgassing, Contamination, and Gas Dynamics

**Moderator:** J.H. Hendricks, National Institute of Standards and Technology

2:00pm **VT-MoA1 A Review of the Development of Cleaning Processes and Cleanliness Assessment at Daresbury Laboratory**, ***J.D. Herbert***, *K.J. Middleman, R.J. Reid, A.N. Hannah*, STFC Daresbury Laboratory, UK **INVITED**

Over the last 30 years the cleaning and processing of vacuum components at Daresbury Laboratory has changed considerably. Although some aspects remain quite similar, others are very different. There are two key reasons for the changes. Firstly, project requirements at Daresbury have changed significantly. Early projects like the Synchrotron Radiation Source (SRS), a 2nd Generation Synchrotron Light Source, required clean Ultra High Vacuum (UHV). Things became more complex when designing DIAMOND, a 3rd Generation Synchrotron Light Source, due to higher photon desorption yields and narrow vacuum chambers. Current projects like ALICE (Accelerators and Lasers In Combined Experiments) and the NLS (Next Light Source) demand vacuum levels in some parts to be in the eXtreme High Vacuum (XHV) region. To achieve this very low levels of contamination are required and very tight restrictions on particles are needed. Secondly, legislation has restricted the range of cleaning processes available. In the early years it was possible to use chlorinated solvents with relative freedom. Environmental legislation then restricted the use of Ozone depleting chemicals and COSHH added further restrictions. Over the last few years both Environmental and Health & Safety legislation has been tightened further. This paper will describe how the vacuum science group at Daresbury Laboratory have adapted to these changes and will describe some of the qualification methods used to determine cleanliness. Also, a recent study of cleaning methods has been conducted, some of the results will be presented and how the results have helped to determine a strategy for the future.

2:40pm **VT-MoA3 The Stainless Steel Bellows with Inner Surface Polishing**, ***O. Koizumi***, Osaka Rasenkan Kogyo Co., Ltd., Japan, *N. Ogiwara*, Japan Atomic Energy Agency, *S. Sawa*, Osaka Rasenkan Kogyo Co., Ltd., Japan, *K. Suganuma*, Japan Atomic Energy Agency, *M. Matsue*, Osaka Rasenkan Kogyo Co., Ltd., Japan

One of the performances required for gas feed system in semiconductor manufacturing equipment is to be particle free. To meet this requirement the inner surface of the bellows must be smoothed and cleaned. This problem for the pipe and mechanical processed parts has been already resolved by combination with electro polishing or electro mechanical buffing, etc., and cleaning. However, for the bellows we could polish the inner surface smooth but not evenly because it is formed in bellows shape. Therefore we established wet mechanical polishing with which it is possible to polish the inner surface of the bellows smooth and even. The feature of this polishing is that you can completely polish the entire inner surface of the bellows by mixing abrasive in the liquid. We finally obtained the inner surface roughness less than Ra=0.05µm for the bellows.Furthermore we realized to be particle free by combing this polishing and cleaning.Also we are planning to report the outgassing rate form the bellows which applied this wet mechanical polishing.

3:00pm **VT-MoA4 A Sensor for Detecting Extremely Low Concentrations of Heavy Hydrocarbons in Vacuum Systems**, ***N.B. Koster***, *R. Jansen*, TNO Science and Industry, The Netherlands

At present vacuum systems are becoming more and more complex and are growing towards a full industrial scale. Together with this growth in size and complexity the cleanliness demands are also becoming more strict. Especially for Extreme Ultra Violet Lithography (EUVL) the requirements on hydrocarbon concentration are high. Typically the total concentration of hydrocarbons in such a tool must be below $1*10^{-12}$ mbar integrated over the mass range 45 to 200 in order to maintain the optics quality during lifetime of the EUVL tool. This also means that the requirements for components and sub-assemblies are even more strict and because the tool cannot be baked the cleanliness has to be verified before integration in the tool. These type of cleanliness demands are also becoming more important for other applications like ALD, CVD, fusion and accelerator systems. We present a sensor, that we are currently developing, that is able to measure the total concentration of heavy hydrocarbons (including fluor compounds) from mass 100 up to infinity in a single channel. The sensor is based on a ionisation source in combination with a magnetic analyser that is used as a low mass filter for removing the species that are of no interest. The masses of interest are led towards a single channel detector for readout of the hydrocarbon partial pressure. Unlike an ordinary RGA the mass range is not scanned but aquired on a single detector, which leads to a significantly higher signal. Also, unlike a RGA, the noise level of the detector is not summed over the scanned mass range, but remains constant. As the sensor is a one channel detector it acts as a Mass Filtered Ion Gauge (MFIG) giving a signal for total concentration of heavy molecules. The benefit of such a sensor is that it gives a single output which enables a go / no go decision for vacuum qualification of chambers and components or in-situ monitoring of contamination levels in a tool. We expect that the sensor has a lower detection limit below $1*10^{-13}$ mbar when operating in faraday mode. The detection limit can be further increased by adding a Secondary Electron Multiplier (SEM) like a Multi Channel Plate (MCP) in front of the faraday detector. This can increase the sensitivity with a factor 100 to 1000. We will present our first results of the sensor when operating at vacuum levels between $1*10^{-6}$ and $1*10^{-9}$ mbar.

3:20pm **VT-MoA5 Low Outgassing, Low Permeability Elastomeric Seals for High Purity PVD Processing**, *G.A. Foggiato, W.B. Alexander*, ***K. Drake***, Greene Tweed Co.

New processes associated with semiconductor manufacturing and in related industries require very clean, high vacuums. Systems utilized for such processes employ a multitude of seals with emphasis in elastomeric seals for transfer handling of substrates. The process environments require such seals to have very low outgassing and low permeability to the atmosphere as well as the gases used in processing. Recent developments of new elastomer seals employing perfluoroelastomers provide the characteristics suitable for these applications. Various material and fabrication technologies are described as used for fabricating seals for high vacuum, ultra high purity environments. This paper will review the new technologies and their effect on the properties of seal materials, the seals themselves and associated equipment performance. Examples of such optimization of seal technology will show the achieved characteristics for seals capable of sustaining vacuums of $10^{-9}$ Torr and at temperatures to 280 $^{o}$C. The outgassing characteristics of a variety of seals will be shown for $H_2O$, HF, H and $O_2$, all potential contaminating gases during depositions of films for semiconductor and photovoltaic thin films. The low level of outgassing attainable by the more recently developed materials and the technology associated with such properties will be described. Through the use of a “tighter” bonding perfluoro molecular structure, combined with molecular based fillers, a molecular structure has been developed which greatly reduces permeability. Through a uniquely developed molding process, key of which is the cooling cycle, a tighter molecular structure is achieved. These new materials provide both the characteristics required for high performance PVD deposition equipment as well as addressing the highly corrosive and aggressive environments found in semiconductor etching and CVD equipment. The progress made in increasing the longevity of seals is such applications is described as this is becoming very critical in future technology nodes manufacturing. Data for use with $NF_3$, $CF_4$ and $O_2$ plasmas is presented to better understand the deterioration of the elastomers and associated mechanisms. The impact of temperature is also described showing that at chamber temperatures approaching 300 $^{o}$C, such new seal materials still function suitably. Descriptions of these extended applications will be given along with the resultant enhanced performance.

4:00pm **VT-MoA7 Novel Leak Testing Methods for High Reliability Hermetic Devices**, ***J.M. Hochrein***, *S.M. Thornberg, J.R. Brown, M.I. White*, Sandia National Laboratories

Traditionally, leak testing is done using helium leak detectors, which are specially designed for the detection of helium. Helium leak tests are often limited to room temperature which does not allow information to be gathered at elevated temperatures. This type of test only provides information about the leak rate under ambient conditions and not about the temperature at which a leak occurs during a thermal profile or how the leak magnitude changes as a function of temperature. In other cases, components may sealed and contain gases that cannot be detected using traditional techniques rendering them ineffective. Two newly developed experimental methods for leak testing high reliability hermetic devices will be discussed. The first method is used to conduct real-time leak monitoring at temperatures ranging from ambient to 900°C while subjecting one side of the parts to continuous vacuum and monitoring for air components. Any loss of hermeticity will result in increases in air components detected. The second method that will be discussed is a method that involves monitoring for the presence of a specific organic target molecule (in this case, a perfluorinated hydrocarbon) to localize the source of a leak. These experiments are conducted at ambient pressure using solid phase micro extraction (SPME) combined with gas chromatography/mass spectrometry.

4:20pm **VT-MoA8 Direct Conductance Measurements of Small Leaks with Simple Geometries**, ***J.A. Fedchak***, *R.F. Berg, D.R. Defibaugh*, National Institute of Standards and Technology

The Pressure and Vacuum Group at NIST utilizes two constant pressure flowmeters as primary standards to calibrate helium leak artifacts, spinning rotor gauges, and ion gauges, using an orifice flow technique. A molar flow rate is produced by allowing gas to leak out of a small volume through a leak valve. By driving a piston into the volume such that the pressure within the volume remains constant, the gas flow rate through the leak valve is determined from the pressure measurement times the volume displacement of the piston per unit time (L/s). In the absence of other sources or sinks of gas, the conductance of the leak is identical to the volume rate of change of the piston. Therefore, the NIST flowmeters can be directly used to measure the conductance of leaks in the range of $10^{-6}$ to $10^{-5}$ L/s. Similar measurements have been done by other labs with primary flow standards (see Jousten et al.,[1] for example), but with limited success due to the inability to accurately model the conductance of leaks with complicated geometries. We directly use the flowmeter to measure the conductance of small leaks with simple geometries, such as thin orifices (OD~10 µm) and capillaries. Small leaks with a known, precisely measured conductance may be used as check standards and in a variety of other applications. The conductance measurements and the applications will be presented.

[1] K. Jousten, H. Menzer, and R. Niepraschk, Metrologia, 39, 519 (2002).

4:40pm **VT-MoA9 Modeling of Diffusion Processes in Vacuum Technology with Finite Element Method**, ***J. Setina***, Institute of Metals and Technology, Slovenia

Diffusion of gasses is a frequent phenomenon in vacuum technology. Examples are: permeation of atmospheric gasses through parts of chamber wall (elastomeric seals and plastics), diffusion of dissolved hydrogen gas in a chamber wall and its evolution into vacuum, and permeation of gasses through membranes in permeation leak elements. The process can be mathematically represented with a diffusion equation, which is a second order partial differential equation. Its solutions depend on the geometry of the system and on initial and boundary conditions. Solutions can be found in analytical form for simple geometries and selected simple initial and boundary conditions only. Diffusion equation can be solved also numerically with finite element method (FEM). Numerical calculations can be applied for arbitrary initial and boundary conditions. In the presentation we will discuss a simple one dimensional case, which can be applied when the problem can be approximated with planar geometry. Numerical calculation of a time dependency of the concentration profile within the sample can be easily performed in a widely use spreadsheet program Excel. The reliability of FEM calculations was checked for a special case of initial and boundary conditions, when the analytical solution is known also. We will also present a practical example of FEM modeling of He gas flow into a vacuum system through a Viton gasket after short-time exposure to He at atmospheric side. Such problem is often observed when He leak detection is performed.

5:00pm **VT-MoA10 Rarefied Gas Flow through a Slit into Vacuum**, ***F. Sharipov***, Universidade Federal do Parana, Brazil, *D. Kozak*, Pontificia Universidade Catolica do Parana, Brazil

The rarefied gas flow through a thin slit represents a great practical and scientific interest. Such kind of flow takes place in many engineering applications, e.g. vacuum equipment, microfluidics, spacecraft design, metrology of gas flow etc. In the present work, such a flow is studied, based on the direct simulation Monte Carlo method. The mass flow rate is calculated with an accuracy of 0.5% over the whole range of the gas rarefaction, from the free molecular regime to viscous one. The flowfield is also provided.

5:20pm **VT-MoA11 Moving Surfaces in DSMC: Implementation, Validation and Applications**, ***R. Versluis***, *M.E. Roos, L. Thielen*, TNO Science and Industry, The Netherlands

Applications in vacuum technology exist where moving surfaces play a role. Under rarefied conditions, moving surfaces influence heat and momentum transfer and surface stress. Several methods have been used to model moving surfaces in Test Particle and Direct Simulation Monte Carlo methods. In simple situations, such as plane Couette flow, one can add an extra velocity vector to molecules hitting a moving surface (the modeled surface stays at rest in an inertial domain). In other examples the flow field is simulated by using a moving calculation domain and the molecule trajectory is corrected for this. Both methods are limited to only one moving surface. But in cases where the domain contains both moving and non-moving surfaces these methods cannot be applied or separate domains need to be defined and the interaction at the interface needs to be prescribed or iteratively determined. We have developed an algorithm to simulate an arbitrary number of moving and non-moving planes in one domain for DSMC methods. The planes can have any velocity vector but should not change the geometry. The method uses periodic boundary conditions (especially implemented for this) and is grid independent. In the DSMC scheme molecule trajectories are determined in two steps: particle movement between collisions and particle collisions. Boundary interaction is taken into account during the particle movement phase. In our method the moving surface is a special boundary with all properties of a normal boundary (temperature, accommodation coefficient, reflection velocity distribution). The difference is that the trajectory of each surface is determined and the exact time and place of interaction between the boundary and a molecule is determined. This way, the exact molecule trajectory is determined during its movement phase taking into account the plane movements during that time. Multiple collisions in one time step between moving and non-moving surfaces are taken into account. The current algorithm is limited to 2D with planes moving in a straight line, but the principle is valid for 3D and planes moving with arbitrary and changing velocities (although the calculation of collisions between plane and molecules becomes more tedious). Results will be shown of validation simulations and possible applications, such as simulations of displacement pumps, moving stages or surfaces in lithography, CVD, PVD and ALD systems, sample manipulation, vacuum conveyor belts etc.

## Applied Surface Science
## Room: 207 - Session AS-TuM

### Use of Cluster Ion Beams for Surface Analysis
### Moderator: M.S. Wagner, Procter & Gamble Company

8:00am **AS-TuM1 Important Variables in Polymer Analysis with Cluster Beams*, C.M. Mahoney***, National Institute of Standards and Technology

Metrology to monitor the surface and in-depth compositions in polymeric materials is important for several applications spanning drug delivery and tissue engineering to microelectronics applications (e.g. photoresists, conducting polymers and dielectric materials). With the advent of cluster Secondary Ion Mass Spectrometry (SIMS), we have shown that one can obtain spatially resolved surface and in-depth molecular information from several polymer systems with depth resolutions on the order of 8-10 nm. However, this technology still has several limitations for polymeric depth profiling. For example, some polymers are more amenable to depth profiling with cluster SIMS than others, while still others experience extensive beam-induced degradation (e.g. polystyrene and polyethylene) resulting in total loss of signal. Described here are our recent efforts at NIST to better understand and define the parameters for successful polymeric depth profiling. For example, temperature has been repeatedly demonstrated to play a crucial role in polymeric depth profiling for both $C_{60}^+$ and $SF_5^+$ sources.[1-3] We also have discovered that different beam chemistries yield different results (e.g. $SF_5^+$ sources has a limited erosion depth as compared to $C_{60}^+$). Other important parameters include oxygen flooding, beam energy and angle, and the stereochemistry of the polymer. Much of what we observe stems from basic radiation chemistry of polymers.

[1] Mahoney, C.M.; Fahey, A.J.; Gillen, G. Anal. Chem. 2007, 79(3), 828-836.

[2] Mahoney, C.M.; Fahey, A.J.; Gillen, G.; Xu, C.; Batteas, J.D. Anal. Chem. 2007, 79(3), 837-845.

[3] Mollers, R.; Tuccitto, N.; Torrisi, V.; Niehuis, E.; Licciardello, A. Applied Surface Science 2006, 252, 6509-6512.

8:20am **AS-TuM2 Expanding the Application of $C_{60}$ in TOF-SIMS Depth Profile Analysis*, G.L. Fisher***, *J.S. Hammond,* Physical Electronics*,* *S. Iida,* ULVAC-PHI, Japan*,* *S.N. Raman, J.F. Moulder, S.R. Bryan*, Physical Electronics

It is acknowledged that atomic ion beams (e.g. $Ar^+$, $Cs^+$ and $O_2^+$) introduce chemical damage to organic materials during depth profile experiments, and the mechanism by which chemical damage occurs is well understood. In the past several years, many publications have demonstrated that buckminsterfullerene ($C_{60}$) ions can be used to successfully depth profile organic materials with minimal accumulation of damage or modification of the chemical composition within the ion beam-exposed region of the material. In addition, depth profiles of molecular ion signals have become much more routine with the use of $C_{60}^+$ ion beams. However, it has been noted in some publications that the sputter rate does not remain uniform through an organic matrix and that efficient sputtering ceases at various depths; such effects are material dependent. The use of higher voltage $C_{60}^+$ beams has extended the range of molecular depth profiling, but changes in sputter rate still occur. These limitations seem to be related, in part or in whole, to either cross-linking of the matrix or accumulation of carbon which reduces the $C_{60}^+$ ion-induced sputter rate. A recent paper by J.-J. Shyue and coworkers has shown that $C_{60}^+/Ar^+$ co-sputtering can be used to extend the depth profile range and maintain a more constant sputter rate.[1] In this paper, we apply the $C_{60}^+/Ar^+$ co-sputtering methodology for TOF-SIMS depth profiling of organic matrices to investigate the effect of co-sputtering on sputter rate, profile range and secondary ion yield.

[1] Y.-Y. Chen, et al., Anal. Chem. 80 (2008) 501.

8:40am **AS-TuM3 Three-dimensional Sputter Depth Profiling of Molecular Structures: Prospects and Limitations*, A. Wücher***, University of Duisburg-Essen, Germany **INVITED**

The use of cluster ions as projectiles in Secondary Ion Mass Spectrometry (SIMS) has opened the door to sputter depth profile analysis of molecular solids. In particular, it is found that molecular information contained in the mass spectrum of material released from the surface by cluster ion impact is retained even if the ion bombarded surface is macroscopically eroded up to micrometers in depth. In combination with finely focused beam probes, high-resolution three-dimensional chemical analysis of molecular structures becomes feasible.[1] This type of experiments, which are virtually impossible using atomic primary ions, bear great implications with respect to biological applications of the SIMS technique. From a number of test studies performed on various model systems, the fundamental principles behind molecular depth profiling are beginning to emerge. The combination of experimental data with phenomenological models and theoretical simulations of the sputter erosion process allows to gain insight into the role of different parameters governing the efficiency of different projectiles for this type of analysis. The talk will briefly summarize the present status of this rapidly evolving field and discuss possible prospects and limitations of the technique.

[1] A. Wucher, J. Cheng, N. Winograd, Anal. Chem. 79 (2007), 5529.

9:20am **AS-TuM5 Comparison of Cluster Ion Sources for XPS Sputter Depth Profiling of Organic Materials*, S.J. Hutton***, *I.W. Drummond, S.C. Page*, Kratos Analytical Ltd, UK

Since the advent of small analysis area (sub millimetre) X-ray photoelectron spectroscopy (XPS) sputter depth profiling has become a standard technique for the characterisation of inorganic materials. Results are produced relatively quickly, interface resolution of multilayer samples is generally good and chemical information can be obtained. Similar XPS sputter depth profiling performance on organic materials is desirable, however, there are several well known problems associated with sputter depth profiling which limit the applicability of this technique to these materials. Some of the most intractable issues are the ion beam induced chemistry often observed during sputtering of polymers and variations in etch rate. The time-of-flight secondary ion mass spectroscopy (TOF-SIMS) community has led the way in addressing these limitations by the use of cluster ion sources. Cluster ions provide a significant increase in secondary ion yield over conventional mono-atomic sources.[1,2] A further significant benefit from this type of source is a reduction in beam induced damage of materials as measured by SIMS.[3] Recently the use of a C60 cluster ion source has been extended to XPS depth profiling.[4,5]The use of this cluster ion source has been shown to also significantly reduce the surface chemical damage of some organic materials during XPS sputter cleaning of materials.[4] This study compares the application of different cluster ion sources for XPS sputter depth profiling of several organic materials.

[1] D. Weibel, S. Wong, N. Lockyer, P. Blenkinsopp, R. Hill, J. Vickerman, Anal. Chem. 75 (7), 1754-1764, 2003.

[2] C. Szakal, S. Sun, A. Wucher and N. Winograd, Applied Surface Science, 231-232, 183-185, 2004

[3] R. Möllers, N. Tuccitto, V. Torrisi, E. Niehuisa and A. Licciardello, Applied Surface Science, 252 (19), 6509-6512, 2006.

[4] N. Sanada, A. Yamamoto, R. Oiwa, Y. Ohashi, Surf. Int. Anal. 36 (3), 280-282, 2004.

[5] Ying-Yu Chen, Bang-Ying Yu, Wei-Ben Wang, Mao-Feng Hsu, Wei-Chun Lin, Yu-Chin Lin, Jwo-Huei Jou, and Jing-Jong Shyue, Anal. Chem., 80 (2), 501-505, 2008.

9:40am **AS-TuM6 The Effect of Cluster Ion Analysis Fluence on Interface Quality in SIMS Molecular Depth Profiling*, C. Szakal*,** National Institute of Standards and Technology*, S. Hues,* Micron Technology*, J. Bennett,* ATDF*, G. Gillen*, National Institute of Standards and Technology

Recent advances in cluster secondary ion mass spectrometry (SIMS) have led to the ability to perform molecular depth profiling for a range of organic materials. Cluster ion beams such as $Au_3$, $Bi_n$, $SF_5$, and $C_{60}$ have shown varying abilities to probe through organic films and soft substrates. The work has been successful because of the premise of sufficiently high target sputter yields that remove beam-induced molecular damage as it is created. Hence, molecular signals can be maintained without significant damage cross sections at ion beam fluences well beyond the traditional "static limit" employed with atomic ion beam analysis. However, in certain modalities, it has been postulated and in some cases demonstrated that a "dual beam analysis" can be exploited for maximum sputtering yield and minimum damage of the erosion beam, while acquiring imaging data with a better-focused smaller cluster beam such as $Bi_n$. This study finds that the effects of the analysis fluence shall not be considered negligible to the imparting of permanent beam-induced damage within the organic materials being depth profiled. Instead, it is found that increasing the analysis fluence can degrade the quality of the interface widths of a high-quality PMMA film on silicon, despite the prospects of the sputter beam to remove accumulated beam-induced damage. The data will be discussed in terms of implications for cluster SIMS molecular depth profiling.

10:40am **AS-TuM9 ToF-SIMS Dual Beam Depth Profiling and Imaging of Human HeLa Cells*, J. Brison***, *D.S.W. Benoit, P.S. Stayton, L.J. Gamble, D.G. Castner*, University of Washington

ToF-SIMS dual beam depth profiling is commonly used in the semiconductor industry to characterize ultra thin inorganic layers with high lateral and depth resolutions (i.e., 300 and 1 nm). This technique, which combines a low fluence ion beam for analysis and a high fluence ion beam for sputtering, is now available to study organic and biological materials using polyatomic primary ions (e.g. $Bi_3^+$ and $C_{60}^+$). However, the more complex and fragile biological materials require special sampling handling to get relevant ToF-SIMS 3D images under UHV conditions. Also, the large ToF-SIMS 3D image data sets present challenges for analysis and interpretation. In this study, human HeLa cells were seeded onto PET substrates, then ToF-SIMS dual beam depth profiles and images of the cells were obtained using 25 keV $Bi_3^+$ (analysis) and 20 keV $C_{60}^+$ (sputtering) primary ions. Different Bi/ $C_{60}$ ion fluences and sample preparation methods (e.g., chemical fixation in 4% PBS paraformaldehyde, vitrification in trehalose, snap-freezing, cryomicrotome sectioning, etc.) were compared and the results were interpreted using principal component analysis. As an example, our results show that for the HeLa cells fixed in 4% PBS paraformaldehyde on PET, $1x10^{14}$ $C_{60}^+$ ions per $cm^2$ are necessary to remove the surface contamination layer so the cell structure could be imaged. After this contamination removal, the high resolution secondary ion images obtained using $Bi_3^+$ primary ions show that morphology of cells is preserved and that intracellular structures can be distinguished and chemically mapped. Our results also show that the interface between the cytoplasm and the PET substrate is reached after $2x10^{14}$ $C_{60}^+$ ions per $cm^2$ while $4x10^{14}$ $C_{60}^+$ ions per $cm^2$ are necessary to reach the interface between the nucleus and the PET. This result indicates that the cell nucleus is significantly thicker than the cytoplasm. Finally, our results show that the intensity of characteristic cell peaks (i.e., the phosphocholine head group from the cell membrane at m/z=184) decrease strongly with the increasing $Bi_3^+$ fluence, indicating that the analysis beam fluence must be carefully controlled to avoid significant chemical damage during ToF-SIMS dual beam depth profiling.

11:00am **AS-TuM10 Strong Field Laser Postionization Imaging and Depth Profiling Using $C_{60}$ Cluster Ion Beams**, ***D. Willingham**, N. Winograd*, The Pennsylvania State University

Laser post-ionization (LPI) of sputtered neutral molecules has been achieved by combining strong field ionization (SFI) techniques with newly developed methods for generating $C_{60}$ cluster ion beams. LPI has been a long desired addition to cluster bombardment experiments for its ability to further enhance the sensitivity of surface measurements. In previous studies, LPI has proven to be beneficial when ionizing atomic species but, problematic when ionizing molecular species.[1] The source of this dichotomy is photodissociation resulting in highly fragmented molecular species. Here we show that by implementing SFI at longer wavelengths the photodissociation of molecular species is greatly reduced, thus vastly improving the efficacy of LPI of sputtered neutral molecules. An important application of LPI is that of chemical imaging using secondary ion mass spectrometry (SIMS). SIMS provides a method for high resolution chemical imaging without the need for sample modification. LPI provides several benefits to SIMS imaging including increased sensitivity, elimination of matrix ionization effects, and an insight into the fundamental properties of the generally undetected sputtered neutral molecules. In addition, SIMS not only provides chemical information in the x and y directions, but due to the development of cluster ion beams may provide chemical information as a function of depth. In past years, sputtering surfaces with $C_{60}$ primary ion beams has proven to be a highly effective method of depth profiling.[2] These advances in cluster ion beams have led to new frontiers for the SIMS community as a whole; however, experimental results are still hampered by matrix ionization effects as well as a fundamental lack of understanding of certain aspects of the sputtering physics associated with depth profiling. LPI finds application here as well providing depth profiles indicative of sputtering dynamics without interference from matrix ionization effects occurring at both the surface and interface regions; and allows for an experimental look at the fundamental physics underlying the sputtering process.

[1] V. Vorsa, et al., "Femtosecond Photoionization of Ion-Beam Desorbed Aliphatic and Aromatic Amino Acids: Fragmentation via a -Cleavage Reactions", J. Phys. Chem. 103(37), 7889 (1999).

[2] J. Cheng and N. Winograd, "Depth Profiling of Peptide Films with TOF-SIMS and a C60 probe", Anal. Chem. 77, 3651-3659 (2005).

11:20am **AS-TuM11 Molecular Depth Profile of Sugar Films: A Comparison Study of C60 Ions and Traditional Cs+ and O2+ Ions**, ***Z. Zhu**, P. Nachimuthu*, Pacific Northwest National Laboratory

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a powerful surface analysis technique because it supplies both molecular information and element information with a reasonable high spatial resolution (~100nm). Furthermore, 3-dimensinal imaging is also feasible. Normally, dual beam analysis strategy I used , in which a second ion beam is applied for sputtering to realize layer-by-layer analysis. Traditionally, low energy Cs+ and O2+ ions are used. However, they are reactive species and organic molecules are easy to be damaged during sputtering process so that only elemental information is collected. Recent years, a new sputtering species, C60 ions were introduced. They are relatively soft and they can sputter materials away with very limited damage so that molecular depth profile can be realized. 3-dimensional imaging of cells and tissues by ToF-SIMS has been of great interest for more than ten years. However, cells and tissues contain a lot of water and they are not compatible with high vacuum environment at room temperature. Immobilizing cells in a sugar matrix has proven to be a good way to resolve this problem. The sugar matrix is stable in vacuum environment. Therefore, the behavior of sugar molecules during ion sputtering is of great important. In this work, we did a comparison study of molecular depth prolife of sugar film on a silicon wafer with C60+, C60++, C60+++, Cs+ and O2+ species. C60n+ species show very exciting molecular depth profile behavior, but Cs+ and O2+ ions seems to damage most of sugar molecules in a short time. X-ray photoelectron spectrometry (XPS) was used to characterize the sputtering craters. The XPS results are well consistent with our ToF-SIMS data.

11:40am **AS-TuM12 Surface Domain Analysis of a Blended Polymer System Using ToF-SIMS**, ***D.D. Wells**, J.A. Gardella Jr.*, University at Buffalo

Biodegradable polymers can serve as drug delivery platforms, thus, understanding the dynamic environment that occurs during degradation, in addition to the static surface chemistry, is crucial to developing better materials.[1] A desirable characteristic of biodegradable polymer materials is the potential for controllable degradation.[2]To that end, this research utilizes time-of-flight secondary ion mass spectrometry to evaluate lateral phase segregation at the surface of a polymer blend. The polymer blend consists of poly(L)lactic acid (PLLA) blended with a fluorine end-capped PLLA (FPLLA) with the expectation that domains of fluorine would appear at the surface. It is anticipated that by controlling domain size, degradation rates within and at the interface of domains can then be spatially tailored. The instrument used in this work is an ION TOF 5.100 equipped with a $Bi_n^+$, $Cs^+$, and $C_{60}^+$ ion source. The spectra obtained from PLLA/FPLLA polymer blends showed the formation of cluster secondary ion repeating patterns in the region from approximately 900 Da to 2100 Da. Results from pure PLLA do not exhibit such cluster ion formation. Images of surface domain formation can be obtained from spatial analysis of the cluster ions from FPLLA even at very low FPLLA blend concentrations (ca. 1% ). Domain sizes at the surface range from 50 to 150 µm diameter. Depth profiles show the results of surface segregation of the end groups and connect to domains within the bulk of the blend.

[1] Ha, C.-S.; Gardella, J. A., Jr., Surface Chemistry of Biodegradable Polymers for Drug Delivery Systems. Chemical Reviews (Washington, DC, United States) 2005, 105, (11), 4205-4232.

[2] Peppas, N. A.; Langer, R., New challenges in biomaterials. Science FIELD Full Journal Title:Science (New York, N.Y.) 1994, 263, (5154), 1715-20.

## Biomaterial Interfaces
## Room: 202 - Session BI-TuM

## Protein and Cell Interactions at Interfaces
**Moderator:** M.R. Alexander, The University of Nottingham, UK

8:00am **BI-TuM1 Multiscale Analysis of Biological Adhesion**, ***D. Leckband**, University of Illinois, F. Li*, Pololu Corp. **INVITED**

In biological systems, the number of protein bonds mediating cell contacts varies from a few for tethering leukocytes to vessel walls to more than 105 in mature cell-matrix contacts. The characterization of the response of single bonds to a dynamic force provides insights into the physics of noncovalent bond rupture, but the more biologically relevant situation involves the rupture of multiple bonds between extended surfaces. A fundamental question concerns how adhesion between parallel surfaces bridged by multiple, parallel bonds scales with the physical chemical parameters of the protein-ligand bonds. Here I describe theoretical and experimental investigations of the forced separation of two adhesive surfaces linked via a large number of parallel noncovalent protein-ligand bonds. Specifically, we consider how the adhesive force scales with bond parameters (kinetics and affinities) as a function of dynamic loading. These results show that the separation rate relative to the intrinsic relaxation time of the bonds defines three loading regimes and the general dependence of the adhesion on kinetic or thermodynamic parameters of the bonds. In the "equilibrium regime", the rupture force asymptotically approaches the "equilibrium rupture force", which increases linearly with the equilibrium bond energy. In the near-equilibrium regime, the rupture force increases with the separation rate and increasingly correlates with the bond rupture barrier, or the logarithm of the dissociation rate. Far from equilibrium where rebinding is irrelevant, the rupture force varies linearly with the rupture barrier, and hence with the bond rupture barrier. Therefore, the adhesive strength of biological interfaces involving multiple, parallel bonds depends on the loading rate, and the loading conditions in turn determine which molecular parameters scale the strength of the junction.

8:40am **BI-TuM3 Molecular Dynamics Simulation of the Adsorption Behavior of Peptides with Secondary Structure to Functionalized Surfaces**, ***G. Collier***, *S.J. Stuart,* Clemson University*, B.R. Brooks,* National Institutes of Health*, R.A. Latour*, Clemson University

While it is well understood that protein-surface interactions are of fundamental importance for understanding cell-surface interactions, very little is understood at this time regarding the molecular level events that control protein adsorption behavior. Molecular dynamics simulations methods have enormous potential for development as a tool to help understand and predict protein adsorption behavior. We are conducting molecular dynamics simulations to simulate the adsorption behavior of peptides with secondary structure to functionalized alkanethiol self-assembled monolayer (SAM) surfaces. Two types of structured peptides are being studied: (1) an alpha-helix forming peptide with a primary sequence of Ac-L-K-K-L-L-K-L-L-K-K-L-L-K-L-NH2 (LKalpha14), where L is leucine (nonpolar amino acid), K is lysine (positively charged amino acid), and Ac represents an acetylated end-group, and (2) a beta-sheet forming peptide, Ac–L-K-L-K-L-K-L-K-L–NH2 (LKbeta9). Two types of SAM surfaces are represented, (1) a CH3-SAM (hydrophobic surface) and (2) a COOH-SAM surface (negatively charged surface). Simulations are performed with the CHARMM force field and simulation package using explicitly represented solvent (150 mM Na+/Cl- in TIP3P water) with periodic boundary conditions. An advanced sampling method, known as replica-exchange molecular dynamics (REMD), is being applied in our simulations to generate Boltzmann-weight ensembles of states for each peptide-SAM system, with the resulting ensembles providing equilibrated structures of peptide behavior, both in bulk solution, and when adsorbed to each type of SAM surface. The resulting ensembles are then analyzed to provide a theoretical understanding of how the surface influences the secondary structure of both the LKalpha14 peptide and a pair of LKbeta9 peptides. In addition, assessment is also being made to quantitatively assess how each SAM surface and the peptide-surface interactions influence the water structure at the interphase region of the system relative to bulk water conditions. Simulation results are being compared with NMR, SFG, ToF-SIMS, and SPR experimental studies that are being conducted in a collaborative effort with Profs. Castner, Gamble, Stayton, and Drobny at the University of Washington.

9:00am **BI-TuM4 Heat Shock Protein Expression and Cell Membrane Study of Printed Chinese Hamster Ovary Cells**, ***X. Cui***, *T. Boland*, Clemson University

Cell printing as a new cell seeding technology in tissue engineering has been attracting more and more attentions. The advantages of high throughput, automatically controlled, low cost of cell printing has a promising future for tissue engineering. Inkjet printing technology is currently widely used for cell printing. However, the heating and stress to the cells during the printing process may cause cell apoptosis or other physical or genetic changes. We present here a comprehensively study of changes in heat shock protein expression and cell membrane morphogenesis in Chinese Hamster ovary cells printed with thermal inkjet printers. We found the optimal cell concentration for cell printing using the modified HP Deskjet 500 inkjet printer using the HP 51626A ink cartridge was one million cells per ml. The heat shock protein expression of the printed cells has minor difference between the untreated cells and lower than manually heated cells. The cell membrane of printed cells developed pores which allow small molecules such as propidium iodide and dextran molecules (up to 70kD) to pass. We conclude here that cell printing technology can be used for precise cell seeding in tissue engineering fabrication with minor effect and damages to the printed mammalian cells. The printing process caused temporary pores with various sizes to appear in the membranes. This may have promising applications for small molecules transferred into cells for protein expression and drug delivery purpose.

9:20am **BI-TuM5 Bioactivity of Adsorbed Protein Layers Correlated with Adsorbed Orientation and Conformation**, ***K.P. Fears***, *R.A. Latour*, Clemson University

It has been well established that protein interactions at biomaterial surfaces are of critical importance because it is the adsorbed protein layer that dictates how the body responds to an implanted material. In general, cells do not have receptors for synthetic materials thus lack the ability to directly respond to non-biological surfaces. Therefore, the critical factors that influence the subsequent cellular responses are the protein comprised in the adsorbed protein layer, their structures, and their bioactivities. Due to the complexity of protein structure and the inherent difficulty of studying surfaces, elucidating the detailed molecular mechanisms involved in protein adsorption is a daunting challenge. We have developed experimental methods to quantitatively assess the secondary structure of adsorbed protein layers using circular dichroism along with the bioactivity of the adsorbed protein layer using spectrophotometric assays. The following model proteins were investigated on alkanethiol (HS-$(CH_2)_{11}$-R, R = OH, $CH_3$, $NH_2$, COOH) modified gold surfaces: hen egg white lysozyme (14.4 kDa, pI ≈ 11, PDB# 1LYZ), xylanase from thermomyces lanuginosus (21.3 kDa, pI ≈ 3.9, PDB# 1YNA), and glucose oxidase from apergillus niger (63.3 kDa, pI ≈ 4.2, PDB# 1CF3). Since CD only provides information about the secondary structure of proteins, amino acid specific chemical modification was used to modify solvent accessible tryptophan residues to provide information about the tertiary structure of the adsorbed proteins and their adsorbed orientations. The results from these studies provide molecular-level insights regarding how surface chemistry influences the adsorbed structure of proteins and how this influences their bioactivity.

9:40am **BI-TuM6 Development of a Novel Biodegradable and Cyto-Compatible Polyurethane for Use as a Bioink in Ink-Jet Printing**, ***C. Zhang***, *N. Brown, T. Boland*, Clemson University

Biodegradable polyurethanes (PUs) were synthesized from methylene di-p-phenyldiisocyanate (MDI), polycaprolactone diol (PCL-diol) and N, N-bis (2-hydorxyethyl)-2-aminoethane-sulfonic acid (BES), serving as a hard segment, soft segment and chain extender respectively. We evaluated the effects of this chain extender on the polyurethanes' degradation rate, mechanical properties, hydrophilicity, antithrombogenecity, and ability to support fibroblast cell attachment and growth. The properties were evaluated by comparing these polymers with those having a 2,2-(methylimino)diethanol (MIDE) chain extender. Mechanical testing demonstrated that the PUs containing BES have tensile strengths of about 17 MPa and elongations up to 400%, higher strength and elongation than PUs containing MIDE. In vitro degradation assays showed the presence of sulfonic acid group decrease the degradation rate of the PU containing BES than that of the PU containing MIDE. Cytocompatibility studies showed that all the PUs are nontoxic, and support cell attachment and proliferation. In vitro platelet adhesion assay showed lower platelet attachment on PU containing BES than that on either PU containing MIDE. Additionally, due to the existence of sulfonic acid groups, the BES extended PU became water-soluble in basic condition and insoluble in acidic condition, a phenomenon that is reversible at pH value of 8.7, making this a pH sensitive polymer attractive for bioprinting applications. By adding acetic acid into an inkjet cartridge and printing it onto basic PU solution, precision fabricated scaffolds were obtained. We will show that these PU scaffolds have preprogrammed pores with fixed sizes of approximately 20 microns. After 5 days cell culture, fibroblasts are seen to attach and proliferate on the porous printed scaffolds, and a number of the cells penetrated into the pores. These results suggest that these PUs are promising candidates as synthetic inks used for customizable fabrication of tissue engineering scaffolds.

10:40am **BI-TuM9 Surface Immobilization and Characterization of Proteins**, *F. Cheng, P.-C. Nguyen, L. Baugh, P.S. Stayton, L.J. Gamble,* ***D.G. Castner***, University of Washington

Immobilized proteins mediate the interactions between a material and its biological environment. We have used XPS, ToF-SIMS, NEXAFS and SPR to investigate protein immobilization onto surfaces containing nitrilotriacetic acid (NTA), N-hydroxysuccinimide (NHS) and maleimide headgroups. NHS surfaces were prepared by self-assembly of NHS ester oligo(ethylene glycol) thiols (NHS-OEG) onto gold. Protein immobilization onto NHS surfaces occurs primarily through the amine groups on the side chains of lysine residues present on the protein surface, resulting in the proteins being immobilized in a random orientation. Mixed monolayers containing NTA headgroups and OEG chains were self-assembled onto a gold surface. The surface concentration of NTA headgroups was 0.9-1.3 molecule/$nm^2$ in the mixed NTA/OEG monolayers, compared to 1.9 molecule/$nm^2$ in pure NTA monolayers. The NTA headgroups were slightly reoriented toward an upright position after OEG incorporation. Histagged, proteins were specifically and reversibly immobilized onto Ni(II)-treated mixed NTA monolayers in well-defined orientations. For a humanized anti-lysozyme Fv fragment the amount of reversible, site-specific adsorption varied from 108 - 205 ng/$cm^2$ with dissociation rates ($k_{off}$) between $1x10^{-4}$ and $2x10^{-5}$ $s^{-1}$, both depending on the NTA surface concentration and orientation. The monolayers without Ni(II) treatment exhibited low nonspecific adsorption. ToF-SIMS was used to compare the controlled orientation of histagged proteins on NTA surfaces with the random orientation of proteins on NHS surfaces. Previously studies have characterized the composition and structure of maleimide-ethylene glycol disulfide (MEG) monolayers on gold for the immobilization of single-stranded DNA oligomers (Lee, et al., Analytical Chemistry 79 (2007) 4390.). These same MEG surfaces were used to covalently immobilize cysteine mutants of the Protein G B1 domain. Two mutants were prepared with cysteines located at opposite ends of the Protein G B1 domain. XPS and SPR were used to quantify the amount of each cysteine mutant onto both bare gold and MEG covered gold surfaces. The ToF-SIMS intensity ratios of amino acid fragments with asymmetric distributions in the Protein G B1 domain (ala, asn, gly, leu, met and tyr) were used to show the two immobilized cysteine mutants had opposite orientations. This difference in orientation was observed on both the gold and MEG surfaces.

11:00am **BI-TuM10 Block-oligonucleotide Brushes: Controlled Structure and Recognition Properties**, *A. Opdahl,* University of Wisconsin*, L.J. Whitman,* Naval Research Laboratory*, **D.Y. Petrovykh***, Naval Research Laboratory and University of Maryland, College Park

DNA brushes with unique properties can be prepared using a new immobilization method that is based on the intrinsic affinity of adenine nucleotides for gold (Opdahl et al., PNAS, 104, 9-14, 2007). The general method uses block-oligonucleotides with sequences that follow a d($A_k$-$T_m$-$N_n$) pattern: a block of k adenine nucleotides [d($A_k$)], followed by a block of m thymine nucleotides [d($T_m$)], and a short sequence of n (arbitrary) nucleotides [d($N_n$)]. These block-oligonucleotides attach to gold via the d(A) blocks and present the rest of the strand for hybridization or for attachment of other molecular recognition ligands. The range of grafting densities produced by this immobilization method can be further extended by co-immobilizing the d($A_k$-$T_m$-$N_n$) probe DNA with short d($A_l$) DNA that act as lateral spacers. We present two applications of this immobilization strategy. In the first, we use d(A) as a means to immobilize d($N_n$) probes for hybridization. We find that the strategy results in reproducible and reversible hybridization behavior, offering practical advantages including low cost and resistance to nonspecific adsorption. Moreover, the high degree of control of probe spacing inherent to the method allows us to observe and quantify by both x-ray photoelecton spectroscopy (XPS) and surface plasmon resonance (SPR) the effects that surface density and conformation of DNA probes have on hybridization efficiencies. In the second application, the d($N_n$) portion of the strand is replaced with a biotin functionality [d($A_k$-$T_m$-biotin)]. Altering the length or mole fraction of the d($A_l$) lateral spacer systematically changes the surface coverage of biotin, allowing control over the amount of streptavidin (SA) that can be linked to the surface. The SA captured by the d($A_k$-$T_m$-biotin) layer is stable and maintains activity towards addition of a subsequent layer of biotin-functionalized molecules. Control experiments also indicate that gold surfaces covered by d(A) oligos exhibit resistance to nonspecific adsorption of SA, both as a molecule and as SA-functionalized microbeads. Since many types of molecules can be functionalized with biotin, compatibility with biotin-SA opens the door to a broad range of applications based on DNA immobilization via d(A) blocks.

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11:20am **BI-TuM11 Surface Initiated Polymer Coatings for the Control of Cell-Surface Interactions**, ***L. Meagher***, *H. Thissen, P. Pasic, R.A. Evans, S. Pereira, G. Johnson, G. McFarland, K. Tsang, T. Gengenbach, K. McLean*, CSIRO Molecular and Health Technologies, Australia

Interest in surface initiated polymerization (SIP) to generate surface coatings for application in biomaterials has increased rapidly in the last few years, particularly those coatings generated using "living" free radical polymerization since they result in coatings with very well defined properties and architectures.[1] Biomaterials applications have largely been in the control of cell attachment, achieved by varying the type of monomer used (e.g. neutral, hydrophilic coatings can be used to reduce protein adsorption and cell attachment). In this study, we present an approach to preparing such coatings which relies on the covalent attachment of a polymer containing controlled free radical initiators onto amine surfaces.[2] This approach allows for maximum flexibility with respect to the substrate (unlike those using self assembled monolayers). Whilst earlier studies have relied on passive coatings, we have included biological signals by building activated functional groups into the coatings as well as drugs and molecules for the specific binding of proteins. These coatings therefore have the potential to interact with biological systems in a much more dynamic manner. XPS and colloid probe AFM were used for coating characterisation. Cell culture studies (24 hours) were carried out with either HeLa, bovine corneal epithelial or L929 fibroblast cells using standard techniques. Protein adsorption was quantified using time resolved fluorescence and proteins labeled with an Eu chelate. Examples presented in this study are the use of iniferters, ATRP initiators and RAFT agents to form SIP coatings with well defined properties. For example, dense polymer brushes which have low or high cell attachment depending on the type and amount of protein adsorption. In addition, the incorporation of cell attachment peptides into coatings via reaction with activated NHS esters will be discussed. Furthermore, the use of click chemistry to conjugate biological signals into coatings formed using our approach will be presented as well as the incorporation of molecules which allow for specific protein binding (e.g. polymerisable biotin) will be discussed in the form of application to ELISAs.

[1] Edmond, S., Osborne, V.L. and Huck, W.T.S. Chemical Society Reviews, 33, 14, 2004.

[2] Meagher, L., Thissen, H., Pasic, P., Evans, R.A., Johnson, G., Polymeric coatings and methods for forming them, WO2008019450-A1, 21 Feb 2008.

11:40am **BI-TuM12 The Effects of Plasma-Polymerized Surface Interactions on R1 Mouse Embryonic Stem Cell Differentiation**, ***E. Hanley***, *J.L. Lauer, G.E. Lyons, J.L. Shohet*, University of Wisconsin-Madison

Plasma polymerized tetraglyme coatings have been studied for their non-fouling and biocompatibility properties due to their inhibition of non-specific protein binding. In this work, we explore how embryonic stem (ES) cell differentiation patterns are affected by surface interactions with various plasma-processed materials. In order to identify a surface as a potential scaffolding material for ES cells in the development of an artificial blood vessel, at least two design criteria must be met. First, the ES cells must adhere to the surface. Second, the surface must facilitate, rather than inhibit, the process of vasculogenesis. ES cells were plated on the following surfaces to compare their effectiveness: 1.) glass cover slips onto which a coating of tetraglyme was deposited by plasma polymerization, 2.) vacuum gas plasma treated polystyrene (Falcon), and 3.) unprocessed control glass coverslips (Corning). In order to characterize the progression of differentiation of the ES cells, each sample was fixed three and seven days after cells had been plated on each surface, and then stained for immunofluorescence analysis. Two genetic markers were used for the antibody staining procedure. PECAM (platelet endothelial cell adhesion molecule: CD31) is an early marker for endothelial cell differentiation. vWF (von Willebrand Factor) is a cytoplasmic protein only expressed in mature endothelial cells. It has been previously reported by using an RT-PCR/southern hybridization blot analysis that ES cells in embryoid bodies first express PECAM near day 5 of differentiation and will first express vWF near day 11 of differentiation. ES cells that were plated on tetraglyme surfaces showed expression of PECAM after 3 days and vWF after 7 days of being plated on the surface. The positive results seen by ES cell derivatives precociously expressing the vWF and PECAM genetic markers on the surfaces suggest a directed differentiation of ES cells into endothelial cells. Furthermore, by using confocal microscopy, it was shown that the endothelial cells that express the vWF genetic marker are those cells closest to the tetraglyme coating. We conclude that the nature of the surface does influence R1 stem cell differentiation. It has also been shown that higher mole fractions of tetraglyme in the plasma during processing increases the percentage of endothelial cell expression.

## BioMEMS Topical Conference
## Room: 309 - Session BM+MN+BI+BO-TuM

## MEMS/NEMS for Biology and Medicine
**Moderator:** E. Meng, University of Southern California

8:00am **BM+MN+BI+BO-TuM1 Microfluidic Systems for Cell Growth and Analysis**, ***K.F. Jensen***, *A. Adamo, L. Ye, Z. Zhang*, Massachusetts Institute of Technology **INVITED**

We present microfluidic systems for cell growth, including instrumented microbioreactors in which the main process parameters (e.g., optical density, dissolved oxygen and pH) are monitored optically and controlled. The system accommodates bioreactors in different operational modes, batch and continuous. The systems are disposable and consist of layers of poly(methyl methacrylate) for structural integrity and poly(dimethyl siloxane) (PDMS) layers for aeration. We also combine cell growth with analysis of protein responses underlying cell signaling. Analysis of these potentially fast transient events requires very short treatment times and well-controlled and reproducible stimulus conditions. Consequently, such pathways can be difficult to probe reproducibly with conventional laboratory techniques that are susceptible to small fluctuations in manual handling – in particular at short times. Microfluidic systems provide for reproducible and automated analysis with excellent control over experimental conditions. We describe microfluidic based methods for investigating signaling pathway ways of adherent cells with the overall aim of controlling cell culture, cell stimulation, and the subsequent protein analysis. The devices, which are fabricated in PDMS by soft lithography, enable dynamic studies of cell signaling by taking advantage of the equivalence between distance travelled along a microfluidic channel and treatment time. They perform all the necessary steps needed in stimulus-signal response analysis of signaling pathways by a fluorescent immunocytochemical assay including cell culture, cell stimulus, cell fixation, and antibody analysis. Average cell population data are obtained by scanning and imaging the entire device, while high resolution microscopy moving along the channel allows responses to be collected at the single cell level. Finally, we present microfluidic devices for quantitative microinjection of macromolecules and nanoparticles into living cells. These approaches overcome limitations with traditional manual manipulation of microinjection needles.

8:40am **BM+MN+BI+BO-TuM3 High-Throughput pMHC Microarrays for Characterizing Diverse T Cell Populations**, ***M. Paulaitis,*** Ohio State University and Johns Hopkins University*, C. Yue, N. Guzman,* Ohio State University*, J. Schneck, M. Oelke*, Johns Hopkins School of Medicine **INVITED**

We are developing protein microarrays for rapidly scanning and screening diverse T cell populations to characterize human adaptive immune responses. An important early molecular recognition event that triggers an immune response is the interaction of a T cell receptor (TCR) on the surface of the T cell with its complementary major histocompatibility complex (MHC) on the surface of antigen-presenting cells. This interaction is mediated by a small peptide (the antigen) 8-10 amino acids in length bound to the MHC, such that the amino acid sequence of the peptide antigen determines the specificity of the TCR/peptide-MHC (pMHC) interaction. Surface plasmon resonance studies of TCR/pMHC interactions have established that the overall range of binding affinities of stimulatory pMHC ligands is low relative to that for anti¬body-antigen interactions. Yet, these interactions have remarkably high specificity/sensitivity leading to T cell activa¬tion and different immune responses depending on the nature of the peptide. Individual T cells are also characterized by a unique TCR; therefore, pMHC microarrays printed with peptides having different amino acid sequences serve to distinguish T cells by their characteristic TCR/pMHC interactions. In addition, co-printing antibodies against cytokines secreted by the captured T cells enables an antigen-specific functional analysis of T cell activation across this population. We show that pMHC microarrays can selectively capture and enumerate antigen-specific T cells in diverse populations at high sensitivity, and that this information provides insights into the general principles governing early molecular recognition events in human immune responses. Results on the functional diversity of the human immune response will also be presented. This work is supported by the National Science Foundation (BES-0555281) and the National Institute of Allergy and Infectious Diseases of the National Institutes of Health (1R21AI077097-01).

9:20am **BM+MN+BI+BO-TuM5 Tunable Microeddies for Microfluidics: Non-contact Single-cell Trapping using Gentle Fluid Flow**, ***B.R. Lutz****, J. Chen, D.T. Schwartz,* University of Washington*, D.R. Meldrum*, Arizona State University

Cells that normally live in suspension typically exhibit strong biological responses to physical contact. Microfluidic devices have been very successful for studying single adherent cells in controlled chemical environments, but tools for manipulating single cells in suspension are extremely limited. We developed a non-contact microfluidic single-cell trap that creates strong trapping forces using only gentle fluid flow. The traps are based on steady streaming flow, which is the steady flow generated when oscillating fluid interacts with any boundary that causes the fluid to turn (e.g., obstacles, cavities, bends). Steady streaming was first identified over a century ago, but its remarkable ability to trap cells was not known. A key feature of this approach is that traps are insensitive to differences in cell shape, cell density, and fluid medium. We demonstrate the ease of trapping for bubbles, spheres, rod-like debris, non-spherical motile phytoplankton, macrophages, and monocytes in different fluid media. The approach is remarkably simple to implement and control, in fact, early work used hand-built flow channels and a home stereo amplifier. The flow is created by audible-frequency fluid oscillation in a microchannel containing a cylindrical post. The back-and-forth motion creates four eddies around the cylinder, and each eddy traps a cell and holds it in place at a predictable location within the fluid. We use capture and release of swimming phytoplankton to estimate the trap strength; strong trapping forces capable of holding the strongest swimmers are easily generated (>30 picoNewtons), while gentle shear conditions in the traps are comparable to arterial blood flow. By using flow to displace trapped spheres under different conditions, we determine a simple scaling relationship that quantitatively describes the trapping force for common cell sizes (5-50 microns). The traps withstand net flows as large as 1 cm/second, which enables medium exchange and chemical treatment of single cells in suspension. Posts can be arrayed with little effect on trapping behavior, providing the potential for high-throughput screening of suspension cells based on dynamic measurements. The combination of strong, tunable trapping forces and gentle trapping environment makes this an appealing new alternative for manipulating single cells in microfluidic devices.

9:40am **BM+MN+BI+BO-TuM6 Automated on-Chip Rapid Microscopy, Phenotyping, and Screening of C. elegans**, ***H. Lu***, Georgia Institute of Technology

Microscopy, phenotyping, and visual screens are critical methods frequently applied to model organisms in combination with genetics. Although widely used, these techniques for multicellular organisms have mostly remained manual and low-throughput. We report the complete automation of sample handling, high-resolution microscopy, phenotyping, and screening of C. elegans using a custom-designed microfluidic system. The engineered system, coupled with customized software, enables high-throughput diffraction-limited imaging and sorting of samples with no human intervention with any microscopy setup. The robustness and automation of our system relies greatly on integrated closed-loop control software as well as engineered hardware design of the microchip. The chip has six salient features that ensure a consistent and reliable operation for an extended period of time. First, it automatically self-regulates the loading of nematodes by a simple passive loading-regulator design. Constant pressure drives the flow, so that no feedback or intervention is necessary for the microchip to allow one and only one animal to occupy the imaging area at a time. Second, the setup automatically positions the samples in an identical position in the chip, so as to minimize the travel of the motorized stage and thereby reduce the processing time and increase the throughput. Third, the device has an integrated local temperature control system whereby animals are cooled to ~4 °C and completely immobilized briefly (~ a few seconds) for imaging and manipulation without the use of anesthetic drugs. Cooling provides an alternative to anesthetics, potentially minimizing the adverse developmental effects. Fourth, the microchip and the setup are compatible with any standard microscopy setup with no modification necessary, including simple compound epifluorescence microscopy, as well as more expensive multiphoton or confocal microscopy. Fifth, the microchip has no permanent small features (<20 μm), and therefore is easy to fabricate, less likely to be clogged by debris, and can operate very robustly. Lastly, losses through our system are minimal (~3%,) and the device design is gentle on the animals as the viability of all the sorted animals is ~100%. We show that compared to standard manual operation, time for phenotyping and visual screens can be reduced by ~2 orders of magnitude in our system with no human intervention, which has not been demonstrated before. Moreover, we show the ability to perform multiple sensitive and quantitative genetic screens with real biological samples based on cellular and subcellular features with over 95% accuracy per round.

10:40am **BM+MN+BI+BO-TuM9 BioMEMS Challenges and Opportunities – A Department of Defense Perspective**, *D. Polla*, Defense Advanced Research Projects Agency, ***S. Barker***, System Planning Corporation **INVITED**

Considerable progress has been made over the last 15 years in realizing a great variety of BioMEMS devices and systems. The field of BioMEMS can be approximately subdivided into three categories: (1) bioanalytical systems, (2), surgical systems, and (3) therapeutic systems. All three areas have numerous commercial and defense applications, but in many cases progress is inhibited by fundamental scientific and technological challenges. This paper presents the authors' perspective on the top 10 challenges facing BioMEMS today. Bioanalytical systems, which are also commonly referred to as "lab-on-a chip," have not realized their full potential for numerous reasons: (1) Autonomous sample processing with minimal human intervention has yet to be achieved. (2) Sample clean-up and pre-processing pose significant challenges that often limit the performance of a bioassay. (3) The ability to take a biological sample and obtain a result or set of results is still a long process, often taking several hours; obtaining a microfluidics-based PCR bioassay result in less than one minute persists as a grand challenge for the BioMEMS community. (4) The development of size-scaled microinstruments for bioanalysis presents an enormous opportunity toward the realization of remote site-derived information that can be conveniently communicated to a physician's office and correlated with a patient's stored medical record. The potential of surgical MEMS has often meant "micro-invasive" surgery that provides significant benefit to the patient. (5) But non-invasive surgery enabled by MEMS has the potential for providing even better patient outcomes. (6) Both sensors and actuators with the capability for more accurately and more reliably reproducing the skill of a surgeon's hands still need to be realized. (7) Developments that enable in vivo imaging of cells and organs using MEMS devices may also play an important role in enabling more effective precision surgeries. Therapeutic systems based on MEMS technology have yet to be made smart. (8) This means effectively integrating sensors, electronics, and actuators in a controlled feedback system designed to provide therapy only when the body needs it. These systems are often implantable and are limited by (9) battery size and lifetime. And finally, (10) neural prosthesis represents an exciting new domain where MEMS may provide an effective interface between nerves and electronics.

11:20am **BM+MN+BI+BO-TuM11 CD Based Sample Preparation and Pathogen Screening**, ***M.J. Madou***, Unversity of California, Irvine **INVITED**

We have demonstrated the feasibility of a multiplexed microfluidic CD apparatus for sample preparation of a wide variety of clinical samples and the subsequent detection of viruses, bacteria and fungi through fast DNA hybridization on the same platform. As the CD slowly rotates, a free moving magnetic disc in a lysis chamber is moved back and forth in the radial direction by the magnetic force of stationary magnets located below the rotating CD. The movement of the magnetic disk causes mechanical shear that disrupts cell membranes. This CD does not only process multiple samples simultaneously, but can also be used for the centrifugal precipitation of solids from each sample liquid. After precipitation, the resulting clarified liquid is transferred through a solid phase extraction membrane to capture the DNA. This step is followed by subsequent automated washing, elution, and detection by hybridization and fluorescence detection on an embedded DNA array. Recent sample to answer results and modeling of ice valves and coriolis valves will be detailed.

## Electronic Materials and Processing
## Room: 210 - Session EM-TuM

### ZnO Materials and Devices
### **Moderator:** J. Phillips, University of Michigan

8:00am **EM-TuM1 Synchrotron-based X-ray Spectroscopy of Transparent Conducting Oxides: ZnO and CdO**, ***L.F.J. Piper***, *A. DeMasi, K.E. Smith,* Boston University, *A.R.H. Preston, B.J. Ruck,* Victoria University of Wellington, NZL, *A. Schleife, F. Fuchs, F. Bechstedt*, Friedrich-Schiller-Universität, Germany

Solids that combine electrical conductivity and optical transparency are essential for today's flat-panel display and solar cell technologies. Post-transition-metal oxides (such as In2O3, ZnO and CdO), with their large band gaps (typically > 3 eV) and ability to sustain high concentrations of electrons with high mobility satisfy this condition. We present recent results from synchrotron-based resonant x-ray emission spectroscopy (RXES) of the O K-edge of ZnO [A. H. R. Preston et al., to be published (2008)] and CdO.[Piper et al., Phys. Rev. B 77, 125204 (2008)]. Bulk sensitive, "photon-in, photon-out" RXES - consisting of both x-ray absorption spectroscopy (XAS) and x-ray emission spectroscopy (XES) - is an alternative to conventional photoemission spectroscopy for examining the valence and conduction band structure of wide band gap semiconductors, such as ZnO. Direct comparisons between RXES spectra and quasiparticle band structure calculations within the GW approximation reveal excellent agreement for both ZnO and CdO.

8:20am **EM-TuM2 Ultrahigh Vacuum Studies of Silane-Functionalized Nanocrystalline and Single Crystal Zinc Oxide**, *J. Singh, J. Im,* ***J.E. Whitten,*** University of Massachusetts Lowell, *J.W. Soares, D.M. Steeves*, U.S. Army Natick Soldier Center

Zinc oxide has a unique bimodal photoluminescence spectrum consisting of UV and visible emission peaks, with the latter believed to originate from surface dependent processes. Possibilities exist to tailor the optical properties of ZnO by appropriate surface functionalization. Adsorption of a variety of silanes on nanocrystalline and single crystal zinc oxide surfaces has been investigated toward the goal of modifying the valence electronic structure and photoluminescence spectrum. Adsorbates include various fluorinated, electron-withdrawing silanes and 3-mercaptopropyltrimethoxysilane (MPS). In the case of nanocrystalline ZnO, adsorption has been carried out from solution, and XPS and FTIR confirm successful covalent attachment to the surface. Comparative studies have also been carried out in which sputter-cleaned ZnO(0001) has been dosed in ultrahigh vacuum (UHV) with model silane molecules. MPS has a high enough vapor pressure to be dosed in UHV, and angle-resolved XPS demonstrates adsorption with the sulfur at the vacuum interface, with minimal polymerization of the MPS monolayer. The effect of coadsorbed water has also been investigated by simultaneously exposing clean ZnO(0001) to water and silane vapors. Ultraviolet photoelectron spectroscopy (UPS) has been used to measure the valence electronic spectra and differences between nanocrystalline and ZnO(0001), and the effect of nanoscale dimensions on the ionization energy of the HOMO valence band (mainly due to nonbonding O 2p orbitals) has been studied. The effects of silane adsorption on the UPS spectra has also been investigated, and attempts have been made to correlate these with changes in photoluminescence.

8:40am **EM-TuM3 Factors Influencing the Formation of Schottky Contacts to Zinc Oxide**, *M.W. Allen,* ***S.M. Durbin***, University of Canterbury, New Zealand

Historically, most attempts to fabricate Schottky contacts to ZnO have resulted in devices with relatively high ideality factors, and barrier heights in the 0.6 – 0.8 eV range regardless of the Schottky metal used.[1] For ZnO applications, such as UV photodiodes, power diodes, and field effect transistors, homogeneous Schottky contacts with low ideality factors, high barrier heights and low reverse leakage currents are required. Recently, significant progress has been made towards understanding the conditions necessary for the reproducible fabrication of high quality Schottky contacts. In particular, studies into the effects of oxidation treatments, such as remote oxygen plasmas, hydrogen peroxide, and ozone, have established the link between improved Schottky contact performance and a reduction in surface hydroxide concentration,[2] while the importance of reducing intrinsic point defects plus additional defects introduced by the metallization process has been established.[3] We have fabricated 'almost ideal' Schottky contacts, with ideality factors approaching the image force limit, on hydrothermally grown bulk ZnO using a number of different Schottky metals. In this paper, we examine the key factors contributing to the success of these contacts. In particular, the polar and non-polar surfaces of bulk ZnO are naturally terminated by a hydroxide layer. Mechanisms for the removal of this accumulation layer are discussed, including the use of a reactive oxygen ambient in the fabrication of silver rich, silver oxide Schottky contacts which produce the highest reported Schottky barriers (1.00 - 1.20 eV) to ZnO. We will also provide evidence for the dominating influence of oxygen vacancies in Schottky contact formation via a relationship between the barrier heights of Ge, Ni, Ir, Pd, Pt Schottky contacts (on the same hydrothermal ZnO material) and the free energy of formation of their metal oxides.

[1] K Ip. et al., J. Crys. Growth 287, 149 (2006).

[2] B. J. Coppa et al., J. Appl. Phys. 97, 103517 (2005).

[3] L. J. Brillson et al., Appl. Phys. Lett. 90, 102116 (2007).

9:00am **EM-TuM4 Metal Contacts to Zn- and O- Polar Bulk ZnO Grown by Vapor-Phase Process**, ***Y. Dong***, *L.J. Brillson,* The Ohio State University, *Z.Q. Fang, D.C. Look,* Wright State University, *D.R. Doutt, M.J. Hetzer, H.L. Mosbacker*, The Ohio State University

Fabricating high quality ZnO contacts remains a challenge and there is little known about the comparison between two ZnO surface polarities (O or Zn-surface) on (i) surface morphologies, (ii) surface defect concentrations and energy levels, (iii) surface reactivities with various metal contacts, and (iv) the Schottky barrier heights and their metal correlations. We used depth-resolved cathodoluminescence spectroscopy (DRCLS), current-voltage and capacitance-voltage measurements, atomic force microscopy (AFM) and deep level transient spectroscopy (DLTS) to probe the possible different behavior of metal contacts to (0001) Zn- and (000-1) O- polar surfaces of high-quality vapor-phase grown ZnO. ZnO (0001) surfaces exhibited higher quality with smaller surface roughness, higher near band edge (NBE) emission and lower surface and near-surface defect emission. Remote O_2/He plasma (ROP) can effectively decrease the 2.5 eV near-surface DRCLS defect emission by removing surface adsorbates and subsurface native defects. Au and Pd diodes in-situ deposited by e-beam evaporation on the ROP treated surfaces can form Schottky barrier diodes (SBDs), while forming good Ohmic contacts on as-received surfaces. The transport properties of the SBDs are not only dependent on metal but also very sensitive to the surface polarities. Generally, gold diodes exhibit better rectifying properties than Pd, while Pd SBDs on the Zn-face have the largest reverse current. This was correlated to the surface morphologies, the DRCLS defect emissions, the CV carrier profiles and the surface and bulk traps revealed by DLTS. The effective donor concentrations for Pd and Au SBDs on the Zn-face were decreased by a factor of ~1.5 than on the O-face in the near surface region, which was accompanied by the higher 2.5eV defect/NBE emission ratio in DRCLS and an additional trap in DLTS for the O-face. The large leakage current for Pd SBDs is due to the sharp increase of carrier concentration at the upper interface region (< 80 nm) and tunneling, especially for Pd SBDs on the Zn face. In addition, for Pd/ZnO(0001) diodes, DLTS identified a new surface trap possibly related to hydrogen at ~0.50 eV below the conduction band and localized within the outer 80-100 nm. Our findings demonstrate the importance of polar effects on forming surface and near-surface defects that control the transport properties.

9:20am **EM-TuM5 Surface and Interface Electronic Properties of Bulk and Epitaxial ZnO**, ***C.F. McConville***, *T.D. Veal, P.D.C. King, S.A. Hatfield,* University of Warwick, UK, *B. Martel,* CNRS, France, *J. Chai, M.W. Allen, S.M. Durbin,* Univ. of Canterbury, New Zealand, *J. Zuniga-Perez,* CNRS, France, *V. Munoz-Sanjose*, Valencia University, Spain **INVITED**

The surface and interface electronic properties of ZnO have been investigated using high-resolution x-ray photoemission spectroscopy (XPS). Understanding the surface and interface electronic properties of ZnO is vital for the realisation of its potential in applications as diverse as gas, chemical and biological sensors, Schottky diodes, light emitters and transparent electrodes. A wide range of ZnO bulk and epi-samples grown by different techniques and with different surface orientations and bulk carrier densities have been studied. These include m-plane and Zn- and O-polarity c-plane hydrothermally-grown bulk ZnO, a-plane and c-plane ZnO grown by metal organic vapour phase epitaxy and c-plane ZnO grown by plasma-assisted molecular-beam epitaxy (MBE). Valence-band XPS indicates that the surface Fermi level is significantly above the conduction band minimum for all of the samples studied, with small variations observed as a function of surface orientation. These results are explained in terms of the band structure of ZnO with its low Gamma-point conduction band minimum, significantly below the charge neutrality level. The results are further discussed in the context of a wide range of previous results on ZnO surface electronic properties, particularly surface conductivity data. Additionally, the first steps towards the development of hybrid oxide/nitride heterostructures have been taken with the MBE growth of ZnO on AlN. XPS has been used to determine the valence band offset of the ZnO/AlN heterojunction. Using the transitivity rule, and our measurements of the III-nitride band offsets, this has enabled all the ZnO/III-N band offsets to be determined. The band offset measurements enable an experimental estimation of the location of the charge neutrality level in ZnO to be made which is found to be consistent with both the observed surface electronic properties and the predictions of band structure calculations.

10:40am **EM-TuM9 Control of Electrical Properties of Atomic Layer Deposition ZnO Channel Layer for Thin Film Transistor: In-Situ Nitrogen Doping and Post-deposition Ultra-violet Treatments**, ***S.J. Lim***, *S. Kwon, H. Kim*, POSTECH, Republic of Korea

For emerging transparent flexible display, ZnO is considered as a promising material for channel layer of thin film transistors (TFTs). For the application, the control of key electrical parameters for the ZnO thin films are required to improve off current (IOFF), on-off current ratio, mobility, and threshold voltage (VTH) etc for ZnO TFT. Atomic layer deposition is one of the promising deposition techniques for the ZnO active layer due to its low growth temperature and good uniformity over large area. However, the control of electrical properties of ALD ZnO for the application of TFT active layer has not been widely studied. In this study, we fabricated the ALD ZnO based TFTs with controlled electrical properties by two ways with low process temperature. First, the in situ nitrogen doping using NH4OH as a reactant was employed to control the electrical properties of thermal ALD ZnO. We effectively reduced the high carrier concentration in ALD ZnO thin films (as high as 1018 cm-3) by nitrogen doping, and obtained low carrier concentration down to 1013 cm-3. High performance inverted staggered type TFTs was fabricated using these nitrogen doped ZnO thin films at low growth temperature (<150 °C), with saturation mobility (µsat) = 6.7 cm2/Vs, on-off current ratio (ION/OFF) = 9.46 × 107, IOFF = 2.03×10-12 A, and subthreshold swing = 0.67 V/dec. In addition, VTH values were controlled by changing the amount of nitrogen incorporation. Second, for plasma-enhanced ALD (PE-ALD) ZnO films has too small carrier concentration in contrary to thermal ALD using oxygen plasma as a reactant. As a result PEALD ZnO TFT does not turn on within voltage sweep range, thus postdeposition ultra-violet (UV) treatments were employed to reduce the carrier concentration. As a result, we obtained proper device properties after UV treatment in vacuum. Additionally VTH of PEALD ZnO TFTs decreased with increasing UV exposure time due to the increment of carrier concentration. We will discuss the effects of nitrogen incorporation and UV treatments on ZnO film properties. Especially, we will focused on demonstrate of the production of ZnO TFTs either depletion mode or enhancement mode controllably.

11:20am **EM-TuM11 ZnO PEALD TFTs and Hybrid ZnO/Organic CMOS Circuits**, ***T.N. Jackson***, Penn State University **INVITED**

ZnO and similar metal oxide semiconductors are of interest because of their wide band gap, transparency, and good electrical transport properties. ZnO thin-film transistors (TFTs) have potential as a higher performance, more stable alternative to amorphous silicon for use in displays and other large area electronics applications. Using ZnO semiconductor and $Al_2O_3$ dielectric layers deposited at 200 °C by plasma enhanced atomic layer deposition (PEALD) we have fabricated n-channel TFTs with field effect mobility > 15 cm$^2$/V-s, subthreshold slope < 100 mV/decade, and current on/off ratio > $10^8$. Seven stage ring oscillators fabricated with 4 µm channel length ZnO PEALD TFTs have propagation delay < 40 nsec/stage for 15 V supply voltage (1.8 MHz oscillation frequency) and oscillate for supply voltage as low as 2 V. CMOS circuits are also of interest, but both p-type doping and p-channel TFTs have been problematic for ZnO. Hybrid inorganic/organic circuits using n-channel ZnO TFTs and p-channel organic thin film transistors provide an alternative path to CMOS circuits. Using Ti/Au contacts treated with a pentafluorobenzenethiol (PFBT) self-assembled monolayer as dual use contacts for both ZnO inorganic TFTs and spin cast difluoro 5,11-bis(triethylsilylethynyl) anthradithiophene (diF TES-ADT, synthesized by J. Anthony, U. Kentucky) organic TFTs, we have fabricated simple CMOS circuits. The diF TES-ADT is simply spin cast onto ZnO devices and Ti/Au contacts in a single step to complete the CMOS circuits. The diF TES-ADT develops a differential microstructure on and near PFBT-treated Au electrodes[1] and allows circuit operation with no direct patterning of the organic semiconductor layer and a simple, four mask CMOS process. The ZnO and diF TES-ADT TFTs used in the hybrid circuits have field effect mobility of 15 and 0.2 cm$^2$/V-s, respectively, and hybrid seven stage ring oscillators with 3 µm channel length have propagation delay less than 200 nsec/stage for 30 V supply voltage. The low temperature processing and good performance of PEALD ZnO TFTs, and the ease of integration with organic TFTs and other devices, make these devices attractive candidates for large area electronic applications.

[1] D. Gundlach et al. Nature Materials, 7, 216–221 (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. Setthapun, 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 19o. 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.

[1] S. 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 phased titania composites were deposited by reactive DC magnetron sputtering. Previously we[1-3] 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 $CO_2$ 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 $CO_2$ reduction. Under UV illumination, the best $CO_2$ 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 $Ti^{3+}$ species in addition to $Ti^{4+}$. Most of the $Ti^{3+}$ 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.

[1] L. Chen, et al., Photoreduction of $CO_2$ by $TiO_2$ Nanocomposties Synthesized through Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2008. in review.

[2] L. Chen, et al., Fabricating Highly Active Mixed Phase $TiO_2$ Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

[3] Hurum, D.C., et al., Probing reaction mechanisms in mixed phase $TiO_2$ 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 $L_3$ edge, were carried out on three different carbon-supported electrocatalysts ($Pt_3Mo$, $Pt_4Mo$, and PtSn) in an electrochemical cell in 1 M $HClO_4$ 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 $Pt_3Ru$) reported previously[1]. The average particle morphology of each catalysts 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, $SnO_n \leq RuO_n$, 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 $H_2$ at low currents.

[1] F. 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 ($CO + H_2O \rightarrow H_2 + CO_2$) 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/$CeO_2$ and Au/$TiO_2$ 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/$CeO_2$(111) or $TiO_2$(110) and inverse $CeO_2$ or $TiO_2$/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-$TiO_2$ (Au/$TiO_2$ and $TiO_2$/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 $H_2$ and $CO_2$. The model Au-$TiO_2$ 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/$CeO_2$ and Au/$TiO_2$ 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 diffences 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 grpahene 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-INFM, Italy, *A. Locatelli, T.O. Mentes, 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 $SiO_2$ 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 $Br_2$-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/$H_2O$ process shows selective deposition of $Al_2O_3$ 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 $Al_2O_3$ layers on top of a HOPG by atomic layer deposition (ALD). The physical properties of the deposited $Al_2O_3$ 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.

## IPF 2008 Frontiers in Imaging: from Cosmos to Nano
## Room: 312 - Session IPF-TuM

### Marine/Terrestrial Imaging
### **Moderator:** D. Zawada, USGS, Florida ISC

8:00am **IPF-TuM1 Imaging in the Underwater Environment: Current Status and Future Trends**, ***S.G. Ackleson***, Office of Naval Research **INVITED**

Natural waters are largely opaque to electromagnetic energy except for a narrow wavelength range between 400 and 700 nm - the visible light spectrum. If the water body, the ocean for example, contained only pure water, it would be possible to view objects through several hundred meters of path length. Unfortunately, natural waters are never pure, but contain large concentrations of suspended and dissolved matter that act to scatter and absorb light energy. The combined attenuation effects of scatter and absorption greatly reduce imaging range. The useful imaging range of conventional camera and flood light combinations is limited to between 1 and 2 optical attenuation lengths, translating to a few tens of meters in clear ocean water, but < 5 m in most coastal and estuarine environments. The development, over the last two decades, of laser-based systems employing synchronous scan and range-gated approaches have increased imaging range to 4 - 5 attenuation lengths and recent improvements in pulsed laser beam form and efficiency and signal processing techniques can potentially increase imaging range another 2 attenuation lengths. However, future improvements in underwater imaging will likely not be driven by better light sources and detectors or sensor architecture, but by how such systems are deployed. Advances in autonomous underwater platforms are allowing imaging researchers to think beyond traditional co-located source and detector approaches to scenarios where the imaging components are distributed within underwater sensing networks. Such approaches could potentially overcome limitations due to imaging range by using knowledge of local environmental variability and may provide opportunities to image across much greater ranges.

8:40am **IPF-TuM3 Coral Fluorescence Imaging**, ***C.H. Mazel***, Physical Sciences Inc. **INVITED**

Fluorescence in corals is optical alchemy, a magical transformation of ultraviolet or blue light to a rainbow of intense hues. Many marine organisms exhibit vivid fluorescence effects, a marvel of physics in action. Photography of coral fluorescence produces images of striking beauty that are also of great value for science. The biological function of the proteins that are the source of the fluorescence is not yet known, although there is no shortage of hypotheses – an aid for photosynthesis of the symbiotic algae, a sunscreen to protect against excessive ambient light levels, a way to preserve and intensify color in the wavelength-limited underwater environment, a beacon for prey. Photographs taken on the reef provide valuable clues that contribute to the scientific sleuthing. Whatever the function of fluorescence for the corals themselves, the phenomenon is a boon for reef science. Juvenile corals are very small (on the order of 1 mm) and are next to impossible to find in the complex surroundings of a reef. By diving at night with the right equipment many of these small corals can be excited to glow brightly, making them easy to find against the darker background. But not even reef scientists want to do all their work at night, and techniques have been developed to find and photograph fluorescing corals in the daytime without special shading. Corals are not the only marine organisms that fluoresce. The more scientists look, the more examples they find over a wide taxonomic range. In some cases the fluorescence signatures are distinct, and work has been done to perform computer classification of seafloor scenes based on the RGB representations of the fluorescence. Imaging is playing an important role in understanding the significance of fluorescence in the marine environment, and in putting the phenomenon to practical scientific use.

9:20am **IPF-TuM5 Deep Sea Bioluminescence**, ***E.A. Widder***, Ocean Research & Conservation Association **INVITED**

Bioluminescence occurs throughout the depth and breadth of the ocean. Organisms use light to find food, attract mates and avoid predators. An overview of bioluminescence will be provided along with an historical synopsis of methods of measurement. Emphasis will be placed on light producers most likely to impact underwater neutrino telescopes.

10:40am **IPF-TuM9 LIDAR in the Coastal Environment**, ***J. Wozencraft***, US Army LIDAR Bathymetry Technical COE **INVITED**

11:20am **IPF-TuM11 Streak-Tube Imaging and the Virtual Periscope**, ***B.E. Hubbard***, Areté Associates **INVITED**

This presentation will survey two distinct types of underwater imaging technology that have been developed in recent years for use by the military community. Areté Associates has developed and patented an innovative LIDAR technology that exploits the high spatial-temporal resolution of a streak-tube to generate extremely high-resolution 3-D images of scenes from a remote platform. This unique approach to 3-D imaging LIDAR enabled unrivaled object detection and classification in turbid media. Since then, Areté has developed several LIDAR systems for the mine countermeasures community that utilizes STIL technology to detect sea mines from air and underwater-borne platforms. Areté Associates' patented Virtual Periscope system enables underwater vehicles to image scenes from below the ocean surface without the need to raise a periscope. This technology improves stealth and mobility of the vehicle and reduces the risk of collisions with surface objects. The Virtual Periscope system uses a compact set of sensors and algorithms to measure and unwrap the image distortions caused by the wavy ocean surface.

## MEMS and NEMS
## Room: 206 - Session MN-TuM

### Materials Processing and Characterization for MEMS/NEMS
### **Moderator:** B.R. Ilic, Cornell University

8:00am **MN-TuM1 Weighing of Biomolecules, Single Cells, and Single Nanoparticles in Fluid**, ***S. Manalis***, Massachusetts Institute of Technology **INVITED**

Recent advances towards developing biomolecular and single cell applications for a mass-based biosensor known as the suspended microchannel resonator (SMR) will be presented. In SMR detection, target molecules or cells flow through a vibrating suspended microchannel and are captured by receptor molecules attached to the interior channel walls. What separates the SMR from the existing resonant mass sensors is that the receptors, targets, and their aqueous environment are confined inside the resonator, while the resonator itself can oscillate at high Q in an external vacuum environment, thus yielding extraordinarily high sensitivity. This approach solves the problem of viscous damping that degrades the sensitivity of cantilever resonators in solution. We have achieved a resolution of approximately 1 femtogram (1 Hz bandwidth) which represents an improvement of six order of magnitude improvement over a high-end commercial quartz crystal microbalance. This gives access to intriguing applications such as mass based flow cytometry and real-time monitoring of single cell growth.

8:40am **MN-TuM3 Development of Superhydrophobic Biomimetic Surfaces with Hierarchical Roughness**, *B. Bhushan*, The Ohio State University, *K. Koch*, Nees Institue for Biodiversity of Plants, Germany, ***Y.C. Jung***, The Ohio State University

Superhydrophobic plant surfaces, e.g. the Lotus leaves, and theoretical calculations show that a hierarchical surfaces roughness is beneficial for superhydrophobicity. Biomimetic hierarchical surface structures were produced by multiple replication of a microstructured silicon master surface. Replicas are made in a two step process, in which a two-component silicon molding mass was applied into the micropatterned Si surfaces, followed by a filling of the mold with an epoxy resin. On these different nanostructures have been applied by physical vapor deposition of hydrophobic n-hexatriacontane ($C_{36}H_{74}$), and octacosn-1-ol. These organic molecules are able to self assembles on the substrates into three-dimensional crystals, and their shape, size and chemistry is comparable to those structures, found on water repellent surfaces. The surfaces created are fully characterized by SEM and AFM and attempted to separate out the effect of hierarchical structures on the hydrophobicity. We show how static contact angles, hysteresis and tilt angles vary with microstructure, nanostructure and hierarchical structure. We also study the effect of droplet size on contact angle by evaporation using droplets on the surfaces.

9:00am **MN-TuM4 Nanomechanical Resonators for Specific Detection of Proteins**, *C. Guthy, L.M. Fischer, V.A. Wright, A. Singh, J.M. Buriak,* ***S. Evoy***, University of Alberta and National Institute for Nanotechnology, Canada

Rapid, sensitive and inexpensive analysis of biological molecules is vital to disease detection, monitoring, drug discovery. For instance, the detection and identification of biomarker proteins of diseases such as metabolic disorders, multiple sclerosis and cancer have gained considerable attention over the recent years. Detection of such proteins with high specificity at very low concentrations would greatly facilitate diagnostic and help predict disease progression. Current analytical technologies such as DNA microarray, mass spectrometry and nuclear magnetic resonance spectroscopy are expensive and technically challenging for clinical applications. Mechanical resonators have been demonstrated as highly sensitive transducers for the detection of molecular systems. The sensitivity of resonators scales favorably as their dimensions are reduced, offering a compelling path for the development of sensors with exceptional mass sensitivities. To enable the specificity of detection, various analyte-specific functional layers need to be immobilized onto the surface of resonators. Such resonators could be then used as sensing arrays for the analysis of complex protein mixtures. As a proof of concept, we recently demonstrated the specific detection of streptavidin using doubly-clamped nanomechanical resonators (bridges) functionalized with biotin. Bridges with widths down to 300 nm were realized from silicon carbonitride (SiCN) thin films using a novel fabrication method. Based on the shift of resonant frequency, a mass of 3.6 fg/$\mu$m$^2$ was attributed to the added streptavidin, corresponding to one molecule per 27 nm$^2$. We have since further scaled down the dimensions of our devices and have demonstrated the surface machining of resonators of world record lateral dimensions of 40 nm with a yield approaching 100%. These 15 µm long resonators show resonance frequencies of ~ 11 MHz with quality factors of ~ 5000 in the mTorr pressure range. We will present a thorough investigation of the resonant behavior of these novel sub-100nm NEMS devices of various dimensions. We are also developing the attachment of antibodies onto these resonators. The specific detection of human interferon gamma (IFN-γ) protein was chosen as target system. Our ultimate goal is to use similar immobilization procedures for the detection of disease biomarkers, including but not limited to multiple sclerosis biomarkers.

9:20am **MN-TuM5 Experimental Determination of the Dynamic Spring Constants of Higher Flexural Modes of Microcantilevers**, ***G. Hähner***, *G.V. Lubarsky*, University of St Andrews, UK

Cantilever based technologies have seen an ever increasing level of interest since the atomic force microscope (AFM) was introduced two decades ago. Most recent developments employ microcantilevers as stand-alone sensors by exploiting the dependence of their oscillating properties on external parameters such as adsorbed mass, or the density and the viscosity of a liquid environment. In this context higher flexural modes have attracted significant attention due to their high sensitivity towards forces and mass changes. While some effort has been devoted to the determination of the static and the first dynamic spring constant, there are currently no equivalent simple yet reliable methods to determine the values of higher modes experimentally. We demonstrate how the spring constants of higher flexural modes of microcantilevers can be determined experimentally with high precision. We recently presented a fast and simple method to measure the dynamic spring constant of the first mode in a non-destructive and non-invasive fashion.[1] The method is based on comparing the spring constants of the cantilever to a known spring constant by measuring the change in the resonance frequency of the flexural modes as a function of the fluid flow through a microchannel. Here we will show that the same approach can also be applied to higher flexural modes. Results for both rectangular and V-shaped cantilevers will be presented and compared to theory.

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[1] G.V. Lubarsky and G. Hähner Rev. Sci. Instr. 78, 095102 (2007).

9:40am **MN-TuM6 Heterodyne Optical Detection of Mechanical Resonances of Ultra High Frequency Silicon Micro-Resonators**, *L.J. Klein,* ***T. Barwicz***, *S. Guha, H.F. Hamann*, IBM TJ Watson Research Center

Recent advancement in microscale electromechanical systems fabrication and operation demonstrated ultra high mass and force sensitivity. Here we investigate the parameters affecting the ultimate sensitivity of suspended mechanical resonators, in particular the resonance frequency and quality factor scaling as the resonators dimensions are reduced. The silicon resonators are fabricated by e-beam lithography with length ranging from 20 um down to 500 nm and having a width of 500 nm. The suspended resonators are actuated using electrostatic force acting between the suspended beam and side gates and an optical heterodyne interferometry is used to detect the resonant oscillations. The heterodyne interferometry has a large bandwidth allowing resonance frequency detection above Ghz and has a detection sensitivity of 10 pm. For fundamental oscillation modes up to 220 MHz, the quality factor of resonance were over 20000 in high vacuum at room temperature and increased in the explored range. We present experimental approaches to detect both flexural and transversal oscillation modes for silicon micro-resonators using our optical detection scheme.

10:40am **MN-TuM9 The Effect of Substrate Material and Metallization Layers on the Mechanical Properties of Micromachined Amorphous Silicon Carbide Structures**, ***R.J. Parro***, Case Western Reserve University, *M.C. Scardelletti, N.C. Varaljay,* NASA Glenn Research Center, *C.A. Zorman*, Case Western Reserve University

Amorphous SiC (a-SiC) films are attractive for micromachined structures requiring the properties of SiC but whose substrates cannot tolerate the high deposition temperatures associated with the conventional CVD methods used to deposit the crystalline forms. The preponderance of data in the literature focuses on the properties of a-SiC films deposited directly onto Si; much less is known about the properties of these films when deposited onto silicon dioxide sacrificial layers. Even less is known about how metallization (required for electrostatic actuation) affects the mechanical behavior of a-SiC micromachined structures. This study examines the roles that the substrate and metallization layers play on the mechanical properties of a-SiC structures. Test specimens were fabricated from 300 nm-thick a-SiC films deposited by PECVD on bare (100) Si wafers and (100) Si wafers coated with a 3.2 um-thick PECVD silicon dioxide film. After deposition, the wafers were annealed at 450C for 30 min to convert the as-deposited compressive film stress to a low tensile stress. Suspended membranes with areas of 750x750 um2 were bulk micromachined by anisotropic etching in KOH at 50C. For the oxide-coated wafers, a 35 min immersion in BOE at 25C was performed to remove the silicon dioxide beneath the SiC membranes. The membranes were subjected to load-deflection testing at differential air pressures between 0 and 138 kPa. From the resulting pressure versus deflection data, it was found that the average Young's modulus for a-SiC films deposited on Si was 129 GPa with a residual stress of 162 MPa, while films deposited on silicon dioxide had a Young's modulus of 116 GPa with a residual stress of 154 MPa. For films deposited on oxide-coated wafers, the effect of metallization on the residual stress of the membranes was characterized. Membranes were first subjected to load-deflection testing, then coated with a Cr adhesive layer and Au structural layer by e-beam evaporation and again subjected to load-deflection testing. For a total metal thickness of 60 nm (10 nm/50 nm Cr/Au), the average residual stress increased by 52 MPa. For a total metal thickness of 125 nm (25 nm/100 nm Cr/Au), the average residual stress increased by 43 MPa, and for 250 nm (50 nm/200 nm Cr/Au) the average residual stress increased by 35 MPa.

11:00am **MN-TuM10 Effects of Actuation Voltage and Relative Humidity on Polycrystalline Silicon Corrosion**, ***F. Liu***, *C.S. Roper, C. Carraro, R. Maboudian*, University of California at Berkeley

The effects of relative humidity and actuation voltage in MEMS have been investigated using polysilicon electrodes. The results indicate occurrence of anodic oxidation under positive bias and absence of cathodic protection under negative bias that leads to the precipitation of dissolved species. We will also report on the effect of electrode geometry and surface termination. Our results show that corrosion can be the dominant failure mechanism of polysilicon MEMS when driven by large electrostatic voltages in humid environments.

11:20am **MN-TuM11 Gold-Tantalum Nanocomposites as Structural Material for Nanomechanical Sensors**, ***N. Nelson-Fitzpatrick***, *C. Ophus, E. Luber,* University of Alberta, Canada, *Z. Lee, V. Radmilovic,* Lawrence Berkeley National Laboratory, *D. Mitlin, S. Evoy*, University of Alberta, Canada

Micro and nanomechanical cantilevers and resonators have received significant attention as a technological solution for ultra-sensitive mass detection.[1] One promising approach to enable specific nanoresonator-based biosensing would be to coat the devices with a thin film of gold in order to exploit thiol-based chemistries for the functionalization of these surfaces. However, such metal coatings would significantly lower its resonance quality, impairing its mass sensitivity.[2] Alternatively, we are currently developing of a novel Au/Ta alloy that would allow the machining of micro and nanomechanical devices directly out of the metal.[3] Metals have been largely overlooked as a structural material for NEMS since most deposition methods tend to yield films with large grain structures complicating reliable machining at the nanometer scale, and containing differential stresses which result in the deformation of released devices. To remedy these problems, we must be able to deposit a metal that is either amorphous or has extremely small grain sizes in order to fabricate a device with nm size critical dimensions. Previously we reported on the deposition of Au/Ta nanocomposites for the purpose of making NEMS resonators.[3] We reliably realized 50nm thick Au/Ta nanoresonators with low stress (~20MPa), reduced grain size and RMS roughness. The devices also retained the gold's <111> texture important for the formation of thiolized SAMs. We have now moved on to the development of micro-cantilevers operating in the static regime with this material. The fine grain size of this alloy enables the realization of ultra-thin, ultra-compliant, released cantilevers directly out of Au/Ta composite. The distinctive grain structure of this material, as well as the inclusion of tantalum impacts the dynamics of molecular attachment, which will affect the response of static cantilevers to the target analyte. To that end, we intend to present a full study on the impact of the alloy nanostructure and its composition on the surface stresses induced by the chemical attachment of a thiolized SAM.

[1] Ilic B, Czaplewski D, Craighead H G, Neuzil P, Campagnolo C and Batt C, 2000 Appl. Phys. Lett. 77 450

[2] Sekaric L, Carr D W, Evoy S, Parpia J M and Craighead H G, 2002 Sens. Act. A 101 215

[3] Nelson-Fitzpatrick N, Ophus C, Luber E, Gervais L, Lee Z, Radmilovic V, Mitlin D, and Evoy S, 2007 Nanotechnology 18.

11:40am **MN-TuM12 Theoretical and Experimental Investigation of Electrostatically Actuated Bistable Micro and Nano Structures**, ***S. Krylov***, Tel Aviv University, Israel, *B.R. Ilic*, Cornell University, *D. Schreiber*, Tel Aviv University, Israel, *S. Seretensky*, Smart Team inc., *H.G. Craighead*, Cornell University

In this work, theoretical and experimental study of initially curved electrostatically actuated micro and nanobeams with clamped ends was performed. Due to unique combination of non-monotonous stiffness-deflection dependence typical for mechanically bistable structures and of nonlinear electrostatic force abundant in micro and nano systems the structure exhibits sequential snap-through buckling and electrostatic pull-in instability as well as multiple stable configurations at the same voltage (bistability). Reduced order Galerkin and consistently constructed lumped models were built and verified by numerical analysis and experimentally. The minimal initial elevation required for appearance of the bistability in the electrostatically actuated beam is smaller than in the case of an uniform deflection independent loading; closed form approximation of this elevation was evaluated. The devices were fabricated from silicon on insulator (SOI) wafer using deep reactive ion etching and in-plane responses were characterized by means of optical and Scanning Electron microscopy (SEM). In addition, out-of-plane moving nano scale devices made of a intrinsically pre-stressed polysilicon were fabricated and characterized. Characterization inside a SEM was found to be a useful experimental approach providing stable operational in-vacuo conditions while higher magnification improves the quality of data processing. Model results obtained for the actual dimensions of the device were in good agreement with the experimental data. Designs incorporating bistable beams have clear functional advantages and may result in improved performance of switches, capacitive based sensors and MEMS/NEMS based nonvolatile memory devices.

## 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 hierarchial 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]

[1] Y. Sugimoto et al. "Real topography, atomic relaxations, and short-range chemical interactions in atomic force microscopy: The case of the Sn/Si(111)-(r3xr3)R30 surface", Phys. Rev. B 73 (2006) 205329.

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

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

[4] N. 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.

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

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

## 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 BCl$_3$-based Plasmas**, ***D. Shamiryan***, 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. BCl$_3$ 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 BCl$_3$-based plasma. Pure BCl$_3$ results in an undercut of TaN. The undercut can be avoided by addition of 5% O$_2$, further increase of O$_2$ concentration (till 10%) does not change the TaN profile. When N$_2$ is added to BCl$_3$ plasma, first the undercut disappears (at about 6% of N$_2$) and then a slope appears as N$_2$ 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 BCl$_3$ 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 O$_2$ 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 BCl$_3$/O$_2$ plasma, attributed to BO$_x$. When 5% N$_2$ is added to the BCl$_3$ plasma, a film of the same thickness as for pure BCl$_3$ is observed, but it contains less Cl (15%). We propose the following etch mechanism. In pure BCl$_3$ plasma a Cl-containing film is deposited on the sidewalls of the gate. Cl from the film reacts with TaN producing an undercut. When O$_2$ 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 O$_2$ content does not change the profile as no film is formed (until O$_2$ concentration reaches 50% when B$_2$O$_3$ film is deposited). When N$_2$ is added to BCl$_3$, a film is formed but in this case N$_2$ replaces Cl and the film becomes passivating leading to a straight TaN profile. As more N$_2$ added, the film passivates TaN more efficiently leading to a sloped profile.

8:40am **PS-TuM3 Etching Profile Simulation of Metal/High-k Dielectric HfO$_2$ in Chlorine Based Chemistry**, ***T. Yagisawa***, *T. Makabe*, Keio University, Japan

With continuous downscaling of complementary CMOS devices, the physical thickness of SiO$_2$ 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/SiO$_2$ with metal/high-k gate stack have been carried out. Among several candidates, HfO$_2$ 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 HfO$_2$ than fluorine chemistry due to the high volatility of the etched by-products. One of the most promising procedures to etch metal/HfO$_2$ gate stack is Cl$_2$/O$_2$ plasma where high selectivity can be obtained over underlying Si and SiO$_2$. 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 HfO$_2$ 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$_x$O$_y$) inside the pattern. Emphasis will also be given on the selectivity of HfO$_2$ etching over Si and SiO$_2$.

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

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* Albert Nerken Award Winner

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 nitrided 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 $BCl_3$ was 4 to 7 times that in $Cl_2$, due to the change in the dominant ion from $Cl_2^+$ to $BCl_2^+$. 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 $Cl_2$ plasmas and the transition between deposition and etching in $BCl_3$ 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 $SF_6/CH_2F_2$ 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 $SF_6/CH_2F_2$ 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 $SF_6/CH_2F_2$ 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 $HBr/Cl_2/O_2$ 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 $SF_6/CH_2F_2$ 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 etching[3] (decreased interaction of charged particles with feature) and UV photon bombardment[4] (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 model[5] 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.

## Surface Science
## Room: 208 - Session SS-TuM

## Dynamics at Surfaces
**Moderator:** A.L. Utz, Tufts University

8:00am **SS-TuM1 Gaede Langmuir Award Lecture: Probing Elementary Process in Chemical Dynamics at Surfaces**, ***D.J. Auerbach****, GRT Inc. **INVITED**

Chemical reactions and energy transfer processes at the gas-surface interface play a vital role in a wide range of scientific and technological problems. In the electronics industries etching and deposition are key steps in the fabrication of microelectronic components. Heterogeneous catalysis lies at the heart of many synthetic cycles in the chemical and pharmaceutical industries. Gas-surface reactions also play an important role in the environment, from acid rain to the ozone hole. Energy transfer at the gas-surface interface influences flight, controlling spacecraft drag, and the

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* Gaede Langmuir Award Winner

altitude of a slider above a computer hard disk. Often such processes involve a complex sequence of events. To develop a molecular level understanding we must find ways to isolate and separately study the elementary processes involved at each step. Molecular beam and laser techniques provide a remarkably rich set of tools to accomplish this decomposition into elementary steps. The method is conceptually very simple. We prepare beams of molecules with well defined properties and scatter these beams for well defined surfaces under UHV conditions. It is possible to control the chemical composition, angle of incidence, kinetic energy, electronic state, vibrational state, rotational state, and even the molecular orientation of the impinging molecules. We then make time resolved observations of the changes in these variables after interaction the surface. The observations provide signatures of the elementary dynamical processes that contribute to a given overall process. They also provide quantitative measures of the rates and cross sections involved and thus provide benchmarks for the development of theory.

### 8:40am **SS-TuM3 Ultrathin K/p-Si(001) Schottky Diodes as Detectors of Chemically Generated Hot Charge Carriers*, H. Nienhaus,*** University of Duisburg-Essen and CeNIDE, Germany*, K. Huba, D. Krix*, University of Duisburg-Essen, Germany

The oxidation of reactive metal surfaces may lead to the emission of photons (surface chemiluminescence) and of electrons into vacuum (exoemission). This is due to the highly non-adiabatic character of the reaction. The exoemission signals are strongly influenced by the change of work function with oxidation and are, therefore, difficult to interpret. Likewise, thin-film electronic devices, e.g. metal semiconductor contacts have been used to detect the internal exoemission by measuring chemicurrents. The internal Schottky barrier acts a high pass energy filter for hot charge carriers. The barrier is much lower than the work function and stays constant during oxidation. Hence, the reaction kinetics may be studied by recording the chemicurrent transients as has been successfully demonstrated for the oxidation of Mg.[1] The interaction of oxygen molecules with alkali metal surfaces is a prototype for charge transfer reactions with strong non-adiabatic energy dissipation. To study the internal exoemission large area K/p-Si(001) Schottky diodes are prepared by evaporation of ultrathin K layers on hydrogen terminated Si(001) surfaces in the thickness range between 2 and 30 monolayers. The metal film growth at low temperatures is monitored by Kelvin probe and Auger spectroscopy. The interface properties are characterized by current-voltage measurements revealing excellent rectifying properties of the diodes. The reverse currents are extremely low and a homogeneous barrier height of approximately 0.56 eV is determined using thermionic emission theory. When the diodes are exposed to molecular oxygen a strong chemicurrent signal is observed. The current increases with exposure time, exhibits a maximum and levels off with large exposures. This behavior indicates a nucleation-and-growth type of oxide formation. The total charge detected in the diode depends on the potassium film thickness in the thin-film regime which allows for an estimate of the oxidation depth.

[1] S. Glass, H. Nienhaus, Phys. Rev. Lett. 93 (2004) 168302.

### 9:00am **SS-TuM4 Vibrationally Hot Precursors – Key Reactants in Catalytic Hydrocarbon Activation?*, D.F. Del Sesto,*** *C.R. Thomas, D. Cook, A.L. Utz*, Tufts University

Gas-surface reactions are often classified as direct or precursor-mediated based on whether their reactivity scales with surface or gas temperature. This interpretation is rooted in the assumption that as gas temperature and kinetic energy increase, trapping probability and hence reactivity for a precursor-mediated process falls. Application of this rubric has led to the conclusion that methane dissociation generally follows a direct mechanism for reaction on a wide range of transition metals. We suggest that this classification scheme might not properly account for the role of a precursor-mediated mechanism that involves vibrationally hot molecules. In this new mechanism, the vibrational energy content (and hence reactivity) of reagents that trap on the surface would also scale with increasing gas temperature, thus clouding the distinction between direct and precursor-mediated mechanisms. If a vibrationally hot precursor mechanism exists, it could well dominate reactivity of important industrial reactions under processing conditions. Relative to the molecules typically studied in beam-surface scattering studies, the methane molecules in an industrial steam-reforming reactor have low translational energy but high vibrational energy. This is because the many vibrational degrees of freedom in a polyatomic molecule can result in a chemically significant vibrational energy content at the elevated temperatures of a steam-reforming reactor. Prior beam-surface scattering studies have not found compelling evidence for this channel in part because the low kinetic energy molecular beams used to ensure adequate trapping probabilities are generally expanded from a room-temperature nozzle source where essentially all molecules are in the vibrational ground state. Studies that quantify vibrational effects in trapping and vibrational quenching on metals, in contrast, do point to a potentially important role for vibrationally excited precursors in catalytic reactions. The presentation will detail this new mechanism for gas-surface reactivity and describe recent results from beam-surface scattering measurements that use both thermal and laser excitation of methane vibrations to assess the importance of this trapping-mediated channel for vibrationally hot molecules.

### 9:20am **SS-TuM5 Photoinduced Electron Transfer Chemistry of $CO_2$ on Pt(111): Dissociation and Desorption following Å–Scale Molecular Acceleration Towards the Surface*, I. Harrison*,** University of Virginia

Ultraviolet photoinduced electron transfer from a low temperature Pt(111) surface to physically adsorbed $CO_2$ is shown to lead to acceleration of the newly formed negative ion towards the surface, neutralization, and a high energy collision with the surface that efficiently dissociates (ca. 30%) and desorbs $CO_2$. The translational energy distributions and angular distributions of photodesorbing $CO_2$ are compared to those of $CO_2$ product from the photoreaction between coadsorbed CO and molecular $O_2$. The similarities of the desorbing $CO_2$ distributions argue for similar exit channel dynamics following access to configurations near the transition state for $CO_2$ dissociation/CO oxidation (i.e., configurations at chemisorptive distances from the surface). Consequently, the initially physisorbed $CO_2$ is accelerated towards the surface following photoinduced electron transfer and can undergo "Antoniewicz bounce" photodesorption dynamics. More interestingly, the initial Å-scale molecular acceleration towards the surface generates molecule/surface collisions at chemically significant energies sufficient to dissociate $CO_2$.

### 9:40am **SS-TuM6 Femtosecond Two-photon Photoelectron Spectroscopic Study of Photodissociation of CFC on Ice-covered Ag (111) Surface**, *S. Ryu, H. Kwon, J. Chang, J. Park, **S.K. Kim***, Seoul National University, South Korea

Solvation and transfer dynamics of photo-injected electrons in thin ice film of water or ammonia co-adsorbed with a CFC (chlorofluorocarbon) molecule such as $CFCl_3$ on Ag(111) have been investigated by time-resolved two-photon photoemission spectroscopy. Water molecules were found to solvate the photo-injected electron within the first several hundreds of fs. The significant lifetime decrease upon adsorption of CFC on the ice film was attributed to dissociative electron transfer of the solvated electrons, based on the observed scission of C–Cl bonds. Furthermore, the photodissociation rate of CFC adsorbed directly on Ag(111) was observed to increase drastically owing to the transfer of the solvated electron when an ice film was overlaid. In the case of ammonia ice film, we found that the lifetime of the solvated electron was much shorter than in water ice. The solvated electron state was found to be located at 2.4 eV above the Fermi level with a binding energy of 0.7 eV at 1 ML of ammonia, and its peak intensity decreased drastically upon increasing the coverage. To shed more light on the excitation process, polarization dependence of the solvated electron peak was thoroughly investigated while modulating the coupling between ammonia and the substrate by use of n-octane as a spacer layer. The observed dynamics of solvation and transfer of electron and the ice layer-induced enhancement of the photoreaction demonstrate the active role of water or ammonia as an electron solvent, which should have far-reaching implications for many electron-driven chemical reactions, including, for example, the newly proposed dissociation mechanism of chlorofluorocarbons by quasi-free or loosely bound electrons on the polar stratospheric clouds.

### 10:40am **SS-TuM9 Dynamics of Analyte Binding onto Metallophthalocyanine Thin Films: NO/FePc**, ***S.R. Bishop****, N.L. Tran, A.C. Kummel*, University of California, San Diego

The investigation of the gas-surface reaction dynamics of NO with different iron phthalocyanine (FePc) thin films utilizing King and Wells sticking measurements is reported. Three surfaces were studied: a flat-lying monolayer FePc/Au(111) film, a crystalline flat lying multilayer FePc film, and a thick amorphous tetra-t-butyl FePc film. The initial sticking probability is a function of both incident molecular beam energy (0.09 – 0.4 eV) and surface temperature (100 – 300 K). For monolayer FePc/Au(111), NO adsorption onto FePc saturates at 3% of a monolayer at all incident beam energies and surface temperatures suggesting that the final chemisorption site is confined to the iron metal centers. At low surface temperature and low incident beam energy, the initial sticking probability is as great as 40% and decreases linearly with increasing beam energy and surface temperature. The results are consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the aromatic periphery followed by diffusion to the Fe metal center. For the multilayer crystalline flat-lying film, the sticking probabilities are greater in comparison to the monolayer for the same incident beam energy and surface temperature, while the saturation coverage for the two films is identical. More efficient trapping onto the crystalline multilayer film is consistent with NO having improved mass-matching with the multilayer FePc surface compared to the monolayer FePc/Au(111) surface. A comparison between sticking to both crystalline and amorphous multilayer thin films is also presented. The initial sticking is similar for the monolayer FePc and amorphous tetra-t-butyl FePc surfaces. Furthermore, the saturation coverage is only 2% for the amorphous multilayer while 3% for the crystalline surface. The reduced saturation coverage in comparison to monolayer FePc is attributed to the reduced coverage of metal centers with the amorphous thin films.

11:00am **SS-TuM10 "Walking Molecules": Symmetric and Asymmetric Species with 1, 2 and 4 Chalcogen "Legs"**, ***G. Pawin***, *K.L. Wong, K.Y. Kwon, L. Bartels, R. Carp, M. Marsella,* University of California, Riverside, *S. Stolbov, S. Hong, T.S. Rahman*, University of Central Florida

Since our discovery of 9,10-dithioanthracene[1] as the first molecule that violates the substrate symmetry in its diffusive motion by perambulating along a single axis on a six-(three-)fold symmetric Cu(111) surface, we have explored this phenomenon extensively and applied it to: (a) transport of cargo,[2] (b) probing of fundamental principles of physics and chemistry, and (c) multi-pronged efforts towards realization of this phenomenon at higher temperatures have been undertaken.

[1] Kwon, K.Y., et al., Unidirectional adsorbate motion on a high-symmetry surface: "Walking" molecules can stay the course. Physical Review Letters, 2005. 95(16).

[2] Wong, K.L., et al., A molecule carrier. Science, 2007. 315(5817): p. 1391-1393.

11:20am **SS-TuM11 Dynamic Processes in Metalorganic Networks Observed by Time-Resolved STM**, ***H.E. Hoster***, *A. Breitruck, R.J. Behm*, Ulm University, Germany

Upon vapor deposition of Cu, hydrogen bonded bisterpyridine (BTP) adlayers on graphite are transformed into hexagonal, long-range ordered metal organic coordination networks.[1] These are stabilized both by hydrogen bonds and metal-ligand interactions. At Cu coverages below phase saturation, we observed the formation of a chiral 2D structure that contains both Cu-free and Cu-containing BTP trimers. The Cu centers themselves are mobile, and their movement within the organic matrix goes along with local re-arrangements of the BTP molecules, which are found to appear only in a finite number of configurations. Under suitable tunneling conditions, the Cu centers are detectable by STM as bright spots. It is therefore possible to quantitatively derive the frequencies of the distinct elementary Cu hopping events by statistical analysis of long STM sequences. We show how the probability of the distinct events can be rationalized by the initial, transitional, and final local configurations of the BTP molecules surrounding the Cu atoms.

[1] A. Breitruck, H.E. Hoster, C. Meier, U. Ziener, R.J.Behm, Surf. Sci. 601 (2007) 4200.

11:40am **SS-TuM12 Control of Scattering Potential for Hot Electrons at Ge(001) Surface**, ***F. Komori***, *K. Tomatsu,* University of Tokyo, Japan, *B. Yan, C. Wang,* Tsinghua University, China, *M. Yamada, K. Nakatsuji*, University of Tokyo, Japan, *G. Zhou, W. Duan*, Tsinghua University, China

Electron scattering in the transport through atomic-scale wires has attracted much interest, especially for possible application to functional devices. We have investigated this subject using a one-dimensional (1D) electronic system at surfaces, where we can study simultaneously the microscopic structure and electron scattering by observing topographic images and electronic standing waves in differential conductance (dI/dV) images with scanning tunneling microscopy (STM).[1] The scattering potential can be controlled by atomic manipulation by STM. Electron scatterings by impurity Si or Sn atoms inserted in a quasi-1D system were studied on a Ge(001) surface at 80 K. On the clean surface, Ge atoms form buckled dimers, which align and form a dimer row. Among the dangling bond states of the Ge dimer, an empty $\pi^*$ surface electron, which localizes at the lower atoms of the Ge dimers, is quasi 1D along the dimer row. We prepared impurity dimers with Si or Sn atoms by deposition on the surface. A buckled Sn-Ge impurity dimer with Sn atom at the lower-atom position (Sn L-dimer) reflects the electrons, and a standing wave was observed in the dI/dV image. Whereas, a standing wave by a Sn-Ge dimer with Sn atom at the upper-atom position (Sn U-dimer) was too small to be observed. The standing wave amplitudes are almost the same for the Si-Ge dimers with the Si atom at the upper- and lower-atom positions (Si U-dimer and Si L-dimer). The signs of the scattering potentials by the impurity dimers were obtained by analyzing phase shift of the standing waves. The Si and Sn L-dimer, where the impurity atom is located in the conduction pathway, are potential well and barrier, respectively, for the $\pi^*$ electrons. Whereas, the Si U-dimer is a potential barrier. These results are qualitatively understood by the fact that the $\pi^*$ electrons propagate on the lower atoms of the buckled dimers. The Si and Sn U-dimer can be reversibly transformed to the Si and Sn L-dimer, respectively, by the bias voltage change for the STM observation as the Ge dimers[2] on the clean surface. Consequently, by switching them between U-dimer and L-dimer, we can manipulate the scattering amplitude of the $\pi^*$ electrons for the Sn-Ge dimer, and the scattering phase for the Si-Ge dimer.

[1] K. Tomatsu et al Science 315 1696, 2007.

[2] Y. Takagi, Y. Yoshimoto, K. Nakatsuji and F. Komori, Surf. Sci. 559 1, 2004; Phys. Rev. B75 115304, 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), $TiO_2$, $Fe_2O_3$ 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 fulfils the requirements imposed by the XRD and HAXPES techniques is presented. The analyzer of the cylindrical sector type[1] 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 $\geq$ 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 (Ekin)$^{0.622}$ 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 luminescene effciency. 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 alighment 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.

## Thin Film
## Room: 302 - Session TF-TuM

### Applications of Atomic Layer Deposition
### Moderator: G.N. Parsons, North Carolina State University

8:00am **TF-TuM1 Atomic Layer Deposition Templating Techniques and Materials for Photonic Crystals*, C.J. Summers*,** Georgia Institute of Technology*, E. Graugnard,* Rollins College*, D. Gaillot,* IEMN Laboratoire Central - CNRS, France*, J. Blair*, Georgia Institute of Technology**INVITED**

Atomic layer deposition is shown to be a powerful tool for the fabrication of novel 3D and 2D periodic dielectric structures. It is a unique complement to a variety of template technologies by providing a mechanism to invert, replicate and convert materials while precisely retaining the form of the original template. The ability to change material type not only enables additional functionalities to be added to the structure, but also significantly enhances the processing range when high melting point materials are substituted for low melting point materials. The ability to refine lattice geometries by the sacrificial layer and backfilling technique are shown to be powerful methods to enhance and tune structural and optical properties. This is demonstrated for both synthetic silica opal and polymer (holographically) derived templates, where dielectric lattice inversion, and the development of large pore structures offer significant enhancement to the photonic band gap by backfilling with different high-index materials. Additionally, the incorporation of luminescent, electro-optic and liquid-crystals can be used to significantly increase the functionality of the original structures. Theoretical and experimental investigations of these structures are presented and provide clear evidence of the precise control enabled by atomic layer deposition. Also we report further extensions of the ALD technique for surface preparation and functionalization for multilayer growth, and developments for the deposition of high index and optically transparent materials such as GaP and Zr3N4. The recent extension of these deposition techniques to the development of novel 2D slab waveguide structures is presented.

8:40am **TF-TuM3 Effect of Yb$^{3+}$ co-Doping on the Luminescent Properties of Er$^{3+}$:Y$_2$O$_3$ Thin Films***, J. Hoang,* ***J.P. Chang***, University of California, Los Angeles

Radical enhanced atomic layer deposition (ALD) has been previously shown to enable the control of the Er$^{3+}$ spatial distribution in Y$_2$O$_3$ thin films, thereby achieving an enhanced direct absorption cross section at 1540 nm and much improved photoluminescence with well-resolved Stark features.[1] Given the larger index of refraction of Y$_2$O$_3$ compared to that of SiO$_2$, this suggests that Er:Y$_2$O$_3$ thin films has the potential to achieve compact optical amplification. In this work, we report the utilization of radical enhanced atomic layer deposition to synthesize controlled concentrations and spatial distances of Yb and Er in Yb$^{3+}$ co-doped Er:Y$_2$O$_3$ thin films and the corresponding improvement in their optical characteristics. The electronic energy level and a large absorption cross section of Yb$^{3+}$ make it an effective sensitizer for Er$^{3+}$. Thin films of approximately 10 nm are synthesized by sequential radical-enhanced ALD of Y$_2$O$_3$, Er$_2$O$_3$, and Yb$_2$O$_3$ at 350°C. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films were determined by x-ray spectroscopy, electron microscopy and photoluminescent measurements. To optimize the effect of the sensitizer and minimize the concentration quenching, the concentration of Yb$^{3+}$ and Er$^{3+}$ were controlled by changing the global deposition cycle sequence. Extended x-ray absorption fine structure analysis verified spatial control of $Yb^{3+}$ and $Er^{3+}$ in the $Y_2O_3$ host. Much improved effective absorption cross sections were estimated using the photoluminescence yield as a function of the pump power, as compared with measurements from thin films without $Yb^{3+}$ sensitizers. From these measurements, an optimum concentration and spatial arrangement is chosen for the design of spiral ridge waveguide devices. These waveguides can achieve potential gains of two orders of magnitude over $Er:SiO_2$ and an order of magnitude over ion implanted $Al_2O_3$.

[1] Hoang, J., T. T. Van, et al. Journal of Applied Physics. 101(12).

9:00am **TF-TuM4 Atomic Layer Deposition of Gallium Nitride Using $GaCl_3$ and $NH_3$ Reactants**, ***O.H. Kim***, *D.J. Kim*, *T.J. Anderson*, University of Florida

GaN films were grown on silicon substrates by atomic layer deposition (ALD) using $GaCl_3$ and $NH_3$. It is postulated that incomplete purging of $GaCl_3$ for long $GaCl_3$ exposure times allows gas phase formation of $(Cl_2GaNH_2)_n$ species with n=1-3,[1] which results in higher chlorine content. X-ray photoelectron spectroscopy was used to determine N/Ga ratio in the film over exposure time, and showed a maximum N/Ga ratio in the saturation limit. Ab-initio calculations were implemented to understand the surface reactions in the saturation limit growth condition. Potential Energy Surface (PES) diagrams for the two adsorption reactions were used to explain the high N/Ga ratio in the ALD limit.

[1] A. Kovács, Inorg. Chem. 2002, 41, 3067-3075.

9:20am **TF-TuM5 Ruthenium and Ruthenium Oxide Thin Films prepared by Atomic Vapor Deposition for MIM Applications**, ***P.K. Baumann***, *C. Manke*, AIXTRON AG, Germany, *G. Ruhl*, Infineon Technologies AG, Germany, *A. Schroeder-Heber*, *L. Pfitzner*, *M. Schellenberger*, Fraunhofer IISB, Germany

As outlined in the International Technology Roadmap for Semiconductors (ITRS), new electrode and high-k materials have to be introduced to replace polysilicon and silicon dioxide, to allow continued scaling of further device technologies. In this study ruthenium and its metallic oxide RuO2 have been examined as possible candidates for MIM (metal-insulator-metal) capacitors. Ruthenium has a low bulk electrical resistivity of 7 microOhmcm. Ruthenium and ruthenium oxide also have very good diffusion barrier properties. We have deposited ruthenium and ruthenium oxide films by AVD (atomic vapor deposition), a pulsed MOCVD (metal organic vapor deposition) method. This method allows to combine features of ALD (atomic layer deposition), such as atomic layer control with the high deposition rate of MOCVD. The electrode films with a typical thickness of 10 nm were deposited on hafnium oxide dielectrics and silicon dioxide as reference. Physical characterization was done by Transmission Electron Microscopy (TEM), Ellipsometry, Atomic Force Microscopy (AFM), and X-Ray Reflectometry (XRR). Near bulk densities of Ru and RuO2 of 12 and 7 g/cm3 have been obtained. For Ru on hafnium oxide a sheet resistance of 10 Ohm/square was achieved. Advanced MIM capacitors were fabricated and characterizes by I vs. U and C vs. U measurements. Even after 5 months storage in ambient conditions the structures showed almost no change in breakdown characteristics. Results from physical and electrical measurements will be presented and correlated. This work was performed within the SEA-NET project funded within the 6th Framework Program of the European Commission, SEA-NET Contract no.: 027982. See www.sea-net.info.

9:40am **TF-TuM6 In-Situ FTIR Study of Atomic Layer Deposition of Ruthenium**, *Y.J. Chabal*, ***S.K. Park***, *J. Kwon*, *M. Dai*, University of Texas at Dallas, *R. Kanjoliab*, SAFC Hitech, *R. Odedrac*, SAFC Hitech Ltd., UK, *N. Boagd*, University of Salford, UK

Ruthenium is a potential capacitor electrode material for DRAMs and FRAMs, and potential gate metal MOSFETs due to is relatively high work function (4.7eV).[1] There is also recent interest in Ru as a combined barrier and seed layer for copper. Since atomic layer deposition (ALD) is technique of choice for deposition of thin and conformal film growth even on structured surfaces such as trenches and via holes, there is an active search for Ru ALD precursors possessing appropriate physical and chemical properties, which are important for the development of a proper deposition process. There is also the need to understand the chemical interaction of these new precursors with various surfaces and the mechanism of ALD growth to advance the field. So far, surface nucleation, overall interface formation and growth mechanisms are not well understood since most of film characterization has been performed with ex-situ measurements. In this study, we present in-situ FTIR studies of ALD growth of Ru thin films on Si substrates using newly synthesized cyclopentadienyl methylruthenium dicarbonyl ($CpRuMe(CO)_2$) and $D_2O$. Film growth rates were determined from ex-situ RBS measurements. $SiO_2$/Si(100) and atomically flat hydrogen-terminated Si(111) surfaces were used as substrates for Ru film growth. For the H/Si(111) substrate maintained at 300°C during growth, the first half-cycle Ru precursor pulse almost completely consumes the surface hydrogen as evidenced by the loss of monohydride Si-H stretching mode at 2084 $cm^{-1}$, which suggests a very high reactivity of the precursor toward the H/Si(111) surfaces at 300°C. The initial Ru deposition on H/Si(111) is initially good at 300°C, then becomes harder (lower growth rate). The precursor reactivity strongly decreases at lower substrate temperatures, involving only 30% of the surface hydrogen at 250°C substrate temperature. More importantly, there is no measurable Ru deposition, presumably because of competitive surface reactions. The reactivity and Ru growth on oxides, specifically $SiO_2$/Si(100) substrate, are surprisingly lower than on H/Si(111) substrates at 300°C. Despite this low growth rate, the IR spectra give clear evidence for ligand exchange and adsorption of surface species, making it possible to identify and quantify surface chemical reactions during the ALD process.

[1] Titta Aaltonen et al., Chem. Vap. Deposition 9, 45 (2003).

10:40am **TF-TuM9 Mechanistic Study of Atomic Layer Deposition of Copper**, ***M. Dai***, *J. Kwon*, Rutgers University, *S.Y. Park*, University of Texas at Dallas, *L.S. Wielunski*, Rutgers University, *Y.J. Chabal*, University of Texas at Dallas, *Z. Li*, *R.G. Gordon*, Harvard University

In microelectronics, Cu is replacing Al for IC interconnects because of its lower resistance and higher melting point. For such microelectronics applications, a controlled metallization method to deposit very thin, uniform and conformal copper films is required. Atomic Layer Deposition (ALD) is the best method but is dependent on the synthesis of appropriate precursors. As recently reported,[1] a novel precursor-Copper(I)di-sec-butylacetamidinate ($[Cu(^{s}Bu\text{-}amd)]_2$)-has shown good performance for ALD of Cu films with high conductivity. Given its novelty and the stringent microelectronics application, it is important to probe the chemistry of both interface formation and thin film growth. We have used in-situ FTIR spectroscopy to monitor the reaction of $[Cu(^{s}Bu\text{-}amd)]_2$ with two types of surfaces, the hydrogen-terminated Si(111) surface and silicon oxide surface, and to probe the next step of the ALD growth ($H_2$ reduction of the adsorbed Cu precursor). The Cu film growth rates were determined using ex-situ RBS measurements. We find that the reactivity of $[Cu(^{s}Bu\text{-}amd)]_2$ on these two surfaces is quite different. H/Si(111) surfaces are less reactive than oxidized surfaces. The IR vibrational spectra show that only ~20% of surface H react at 185°C. RBS measurements indicate that only 0.09 nm of Cu grows on H/Si(111) after 10 cycles. In contrast, there is a substantial loss of the $SiO_x$ TO and LO phonon mode intensity at 1075$cm^{-1}$ and 1247$cm^{-1}$ after the 1st Cu precursor pulse at 185°C on $SiO_2$ surface, indicating that the surface $SiO_2$ matrix chemically interacts with the precursor. Meanwhile, a broad absorption band centered at 1010$cm^{-1}$ is observed, corresponding to the formation of Si-O-Cu bonds. Upon $H_2$ exposure, the intensity of the $SiO_x$ phonon modes is partial recovered, suggesting that Cu atoms diffuse and agglomerate as the Cu precursor is reduced to pure Cu at 185°C. As agglomeration takes place (i.e. Si-O-Cu bonds are broken), the initial hydroxylated oxide surface is restored (in a hydrogen environment) and is characterized by the original $SiO_x$ phonon absorption. The ALD process is investigated by following the ligand exchange and ligand rearrangement on the surface. RBS measurements show 1.18nm of Cu is deposited on $SiO_2$ after 10 cycles.

[1] Z. Li, S. T. Barry, R. G. Gordon, Inorganic Chemistry, (2005)44, 1728.

11:00am **TF-TuM10 Modification of Nonwoven Polymer Fiber Structures by Atomic Layer Deposition**, ***J.C. Spagnola***, *G.N. Parsons*, North Carolina State University

Nonwoven polymer fiber structures are receiving much recent attention due to their potential industrial, medical, and military applications. We report the modification of nonwoven fiber structures by the deposition of thin metal oxide films via ALD. Fiber substrates coated to date include melt blown polypropylene micro and nanofibers, electrospun PVC nanofibers and nylon hydroentangled microfibers. Our specific focus is to characterize the effect of film thickness and/or coating material the resulting mechanical properties of coated fiber structures Initial experiments involved the deposition of Al2O3 by trimethylaluminum and water at temperatures from 50 to 100C. The gas pulse and purge times used resulted in film growth rates of 1.2A/cycle on planar silicon independent of temperature. Substrates for ALD coating consisted of fiber mats approximately 1cm x 3cm x 0.05cm. After ALD, some samples were calcined in air at ~850°C for 30 min to remove the polymer substrate to allow SEM analysis of the deposited oxide layer. SEM images show good macroscopic uniformity of the ALD coating over the substrate surface area. Other samples that were not heat treated were analyzed under tensile testing to observe the stress-strain behavior as a function of ALD process conditions and film thickness. Specifically, melt-blown polypropylene nonwoven fiber mats were tested using a microstrain analyzer to determine elastic modulus, yield stress and material toughness. Coating the polypropylene with Al2O3 ALD at 50°C or 100°C lead to an increase in the elastic modulus that scaled linearly with the number of ALD cycles, resulting in an increase of ~50% after 200 ALD cycles (~25nm). In addition, when the ALD was performed at 50C, the samples showed an increase in yield stresses with some improvement in material toughness. However, when processed at 100C, the coated polypropylene structures showed a decrease in yield stress and toughness as compared to untreated substrates, consistent with some degradation of the starting material properties at elevated temperature. Strengthening of the fiber structure by the deposition of a thin metal-oxide film may allow coated nonwovens to be used in applications where the traditional low-strength of nonwoven structures prevents the required level of performance.

11:20am **TF-TuM11 Mechanical and Tribological Property Comparison of Melt-Compounded Nanocomposites of Atomic-Layer-Deposition-Coated Polyamide Particles and Commercial Nanofillers**, *K.M. Nevalainen, R.J. Suihkonen,* Tampere University of Technology, Finland, ***N.A. Isomäki***, Beneq Oy, Finland, *C. Hintze,* Technical University of Chemnitz, Germany, *P.S. Eteläaho, J.E. Vuorinen, P.K. Järvelä*, Tampere University of Technology, Finland

A recently developed process to form homogenously dispersed nano-sized titanium dioxide ($TiO_2$) particles within a polymer matrix was introduced and compared to traditionally melt-compounded nanofillers. Micron-sized polyamide particles were pre-coated with thin $TiO_2$ films by atomic-layer-deposition (ALD). ALD coating was performed at 40 °C by alternately exposing polyamide powder to titanium tetrachloride and water, separated by nitrogen purge steps. $TiO_2$ coatings on polyamide particles possessed nominal thicknesses of 10 nm or 40 nm. The ALD-coated polyamide particles and the composites manufactured from the two different commercial $TiO_2$ nanofillers were melt-compounded using a 5 $cm^3$ micro-compounder. The dispersion of the crushed $TiO_2$ shells in the polyamide matrix were studied after extrusion using a transmission electron microscopy and the results suggested very different morphology from the traditional $TiO_2$ nanocomposites. The ALD-created $TiO_2$ appeared as ribbons in the polyamide matrix whereas the commercial $TiO_2$ fillers formed spherical clusters. The effect of these $TiO_2$ morphology changes on the mechanical response of the specimens subjected to tensile and impact loading was investigated. The results demonstrated that the nanocomposites based on ALD-coated polyamide particles possess 50-150% higher Young's modulus than pure and commercially filled polyamide matrix whereas yield strength is only slightly increased for 10 nm ALD-coated composite and in fact somewhat decreased for 40 nm ALD-coated composite. Furthermore, the ductility upon tensile loading is significantly affected. A transition from ductile to brittle deformation occurs for both ALD-coated nanocomposites. Notched impact strength experiments supported this phenomenon showing that the impact strength of ALD-coated composites decreased 50% compared to pure and traditionally filled polyamide matrix whereas the traditional $TiO_2$ nanocomposites showed no significant changes. The fracture surfaces of the nanocomposites examined with scanning electron microscope suggested that the nanoparticle dispersion was good but some impurities in the matrix were found and their origin is discussed. The tribological properties of the selected specimens were also determined using pin-on-disc type apparatuses and the effect of the titanium dioxide fillers on the friction and wear properties of polyamide matrix is examined.

11:40am **TF-TuM12 Atomic Layer Deposition of Zinc Hybrid Films from Diethyl Zinc and Ethylene Glycol**, *Q. Peng, R.M. VanGundy, G.K. Hyde,* ***G.N. Parsons***, North Carolina State University

Atomic/molecular layer deposition of organic-inorganic hybrid materials could significantly expand the range of materials available in thin film applications. However, the detailed mechanisms associated with the integration of organic materials into the ALD process scheme need to be more fully understood. In this study, zinc hybrid films were formed by atomic layer deposition using alternative dosing of diethyl zinc (DEZ) and ethylene glycol (EG). The process was characterized using in-situ quartz crystal microbalance (QCM), as well as a range of external characterization tools and results were compared directly to the ZnO ALD process (DEZ/H2O) performed under similar reaction conditions. Consistent with literature results, during the ZnO ALD process at 120degree C, the mass uptake during the DEZ exposure is ~130 ng/cm2 per cycle, with a small mass loss during H2O exposure. The QCM results confirmed the self-limiting surface adsorption during both reaction steps of ZnO ALD. When H2O is replaced with ethylene glycol in the process sequence at 120 degree C, the mass uptake during the DEZ pulse is reduced significantly to ~19 ng/cm2 , and the positive mass uptake of ~ 4 ng/cm2 is observed during the EG pulse in the steady-state deposition of Zn hybrid. The reduced mass uptake during DEZ exposure is likely due to the lower density of reaction sites resulting from: (i) the twice reaction of EG with surface bonded –O-Zn-C2H5 ligands; (ii) steric hindrance of bulky EG molecules and its related surface bonded ligands; (iii) the possible dehydration reaction between the surface bonded EG ligands. Self-limiting adsorption of DEZ and EG, which is consistent with a typical ALD process, was confirmed by QCM. The process steps of Zn hybrid can continue for several hundred cycles with consistent and repeatable mass uptake. The growth rate per cycle of the hybrid material decreases as the deposition temperature increases. Infrared analysis of as-formed Zn hybrid films shows modes consistent with EG and Zn-O bonds. Upon exposure to laboratory air, the resulting hybrid films readily undergo hydrolysis, resulting in films consisting of ZnO and hydroxide with significant carbon content, as evidenced by FTIR and XPS analysis. AFM shows the films are uniform, and TEM analysis indicates that hydrolysis process results in conformal and porous layers. Further results of in-situ characterization and post-deposition analysis of the zinc hybrid materials will be presented.

## Vacuum Technology
## Room: 205 - Session VT-TuM

### Vacuum Pumping Technologies, Large Vacuum Systems, Vacuum Modeling
**Moderator:** M.L. Stutzman, Jefferson Lab

8:00am **VT-TuM1 Modeling a Turbomolecular Pump with Direct Simulation Monte Carlo (DSMC)**, ***M.E. Roos***, *R. Versluis, L. Thielen*, TNO, the Netherlands

Three flow regimes can be distinguished (ordered in decreasing pressure): the continuum regime, the transitional or rarefied regime and the molecular regime. Modeling of the continuum flow regime is covered by Computational Fluid Dynamics. The fluidum is regarded as a continuum and the discrete character of molecules is not taken into account. For the molecular regime network modeling can be applied. This is the equivalent of electric network modeling applied to flows. It has always been a problem to model the transitional regime. Transitional flow conditions appear in a wide range of applications where vacuum is applied or small dimensions prevail. Some examples: the design of precision instruments (newest generation lithography machines), physical and chemical vapour deposition processes (fabrication of solar cells or coating of metals) or space technology (plume from a rocket nozzle). TNO has developed in cooperation with the Delft University of Technology a tool to model the transitional regime. This tool is based on the Direct Simulation Monte Carlo (DSMC) method. In this model flow properties are determined by simulating the movement and collisions of molecules. A mixture of different gases can be modeled as well as chemical reactions between gases and on surfaces. The DSMC model is implemented in the parallelized numerical 3D flow solver CVD-X (developed in-house by TNO). The DSMC model is also valid in the molecular and continuum regime. The development of the model is an ongoing process. Recently the model has been extended to be able to simulate moving parts in the transition regime. In our method moving parts are implemented as special boundaries which are moving through the domain. A moving boundary has all properties of a normal stationary boundary (like temperature and accommmodation coefficient). In addition the exact time and position in space of the interaction between molecules and a moving boundary is determined throughout time. Multiple collisions of molecules in one time step with moving and non-moving surfaces are taken into account. This method makes it e.g. possible to model the spinning rotors of a turbomolecular pump and optimize the efficiency. We are performing DSMC simulations on a turbomolecular pump using this method. The results of these simulations and the validation with experimental data are presented.

8:20am **VT-TuM2 Evaluation of Metallic Films of TiZrV and Au used in Ultra-High Vacuum**, ***M.J. Ferreira***, *R.M. Seraphim,* Brazilian Synchrotron Light Laboratory - LNLS, *P.A.P. Nascente*, Federal University of Sao Carlos - UFSCAR, Brazil

The construction of ultra-high vacuum chambers (UHV) for particle accelerator demands pressure in the range of $10^{-8}$ Pa. It is particularly more difficult to obtain this vacuum level in chambers with a length to traverse section rate of 150:1. Among several methods used to obtain this condition, it stands out the internal coating with a metallic film capable of absorbing gases, called NEG (non-evaporable getter). Metallic films used in synchrotron accelerators cannot have gas molecules adsorbed on the surface and should be deposited on the internal surface of the chamber, making it a vacuum pump. Usually these materials are constituted by elements of great reactivity and solubility (such as Ti, Zr, and V) at room temperature, for oxygen and other gases typically found in UHV ($H_2$, CO, and $CO_2$), besides having considerable diffusibility at low temperature (< 700 K), the so-called activation temperature. The objective of this work is to prepare and evaluate films of TiZrV alloy and Au produced by magnetron sputtering. The film structure, morphology, and aging have been characterized in order to know how much of the gas absorption property at low temperature can be attributed to the chemical reactivity of the elements and to the structure formed by the deposition process. The morphological, structural, and chemical characterization was carried out by atomic force microscopy (AFM), high-resolution scanning electron microscopy (FEG-SEM), energy dispersive spectroscopy (EDS), X-ray diffraction (XRD), and photon stimulated desorption (PSD). The produced materials were compared with commercial TiZrV samples, and this comparison made clear that the desired characteristics are related to the nanometric structure of the films and that the structure is clearly sensitive to the heating treatments.

Acknowledgements: we would like to thank Vinicius L. Pimentel and Roosevel Droppa Jr. for their assistance on some of the experiments.

8:40am **VT-TuM3 Sorption Properties of Non Evaporable Getter Pumps for Selected Hydrocabons and Organic Compounds*, A. Conte***, SAES Getters S.p.A. Italy **INVITED**

Non Evaporable Getter (NEG) pumps are very clean, vibration-free, compact UHV pumps able to deliver large pumping speeds for all active gases, including water and hydrogen. Plenty of literature is available describing the sorption characteristics of NEG pumps toward the gases typically present in UHV system, e.g. hydrogen, carbon oxides, water, nitrogen and oxygen. Fewer papers can be found describing the behaviour of NEGs toward hydrocarbons. Most of the experimental data available in the literature are related to pumping of methane or relatively simple hydrocarbons like the lower alkanes. Very few data are available for more complex molecules. On the other hand, pumping of volatile and organic compounds is an issue in a variety of vacuum applications , especially those related to silicon and semiconductor materials processing, wafer in-line inspection, e-beam and Extreme Ultra Violet Lithography (EUVL). In the present study we report the results of specific tests aimed at measuring the pumping speed for some selected organic compounds, namely toluene, decane and methyl methacrylate (MMA). The study shows that NEG pumps can effectively sorb these large organic molecules with high speed and capacity even at room temperature. This opens up the possibility of using NEG pumps in combination with other typical UHV pumps in those systems were organic volatile compounds can be present to improve the ultimate vacuum and mitigate the carbon/oxygen contaminations.

9:20am **VT-TuM5 New Methods to Achieve XHV/UHV with Refrigerator Cooled Cryopumps**, *B. Rock*, ***D. Muller***, *M. Ahlers*, *T. Brown*, Oerlikon Leybold Vacuum

Cryopumps have a higher effective pumping speed compared to ion pumps or turbomolecular pumps, especially for the typical gasses which limit the ultimate pressures in UHV devices like water vapor or Hydrogen. In addition, they are absolutely hydrocarbon free. The ultimate pressure of commercial refrigerator cooled cryopumps is mostly limited by 2 factors: they cannot be baked completely and they cannot be operated while attached to a chamber during bakeout due to the high thermal load. This paper presents a simple modification of a standard cryopump including the ability to cool the radiation shield with LN2 during bakeout. Pressures below 1 X $10^{-12}$ mbar have been reached even in larger vacuum chambers. The possibilities to measure these pressures via the Extractor gauge are shown too.

9:40am **VT-TuM6 The KATRIN Experiment: Vacuum Performance of the Large Main Spectrometer Vessel*, J. Wolf***, Universität Karlsruhe, Germany

The scientific objective of the KArlsruhe TRItium Neutrino experiment (KATRIN) is to measure the electron neutrino mass from the β-decay of tritium with an unprecedented sensitivity of 200 meV/$c^2$. The kinetic energy of the decay electrons will be measured by an electrostatic spectrometer. Background considerations require a very good vacuum of $10^{-11}$ mbar or better in the large spectrometer vessel (volume 1240 $m^3$, surface: 690 $m^2$). A combination of NEG pumps ($S = 10^6$ l/s) and turbo-molecular pumps will provide the necessary pumping speed. In addition a very clean surface and low outgassing rates are mandatory. This talk reports on the manufacturing, vacuum performance before and after bake-out at 350°C.

10:40am **VT-TuM9 LHC Beam & Insulation Vacuum Systems*, J.M. Jimenez***, CERN, Switzerland **INVITED**

In May’08, the world largest vacuum system was fully commissioned and consolidated in the Large Hadron Collider (LHC), a CERN accelerator built near the City of Geneva in Switzerland. Its more than 100 km of vacuum systems are operating over a wide range of pressures and integrates an impressive variety of vacuum technologies. These vacuum systems are composed of 54 km of UHV vacuum for the circulating beams and two times 24 km of insulation vacuum around the cryogenic magnets and for the cryogenic helium transfer lines. 48 km out of the 54 km are operated at a cryogenic temperature (1.9 K). The remaining 6 km of beam vacuum containing the insertions is at ambient temperature and uses non-evaporable getter (NEG) coatings, a vacuum technology that was born and industrialized at CERN. The pumping is completed using 600 ion pumps to remove noble gases; 1000 gauges are used to monitor the pressures. The cryogenic insulation vacuum of the magnets, while technically less demanding, impresses by its 24 km in length and a diameter of 900 mm for a total volume of 640 m3. Once cooled at 1.9 K, the cryogenic pumping allows reaching pressure in the 10-6 mbar range. This talk will introduce the vacuum systems and the challenges of its design, manufacturing, installation, commissioning and consolidation phases.

11:20am **VT-TuM11 The Modeling of Large and Distributed Vacuum System*, A.D. Chew***, *M. Galtry*, *J. Luby*, Edwards, UK

As the size and complexity of vacuum systems increases the financial and technical challenges do so also. Accurate modeling allows system optimisation in advance of engineering efforts and negates the need for inefficient empirical iterations. This paper will describe a computational modeling technique which allows the modeling of vacuum systems incorporating any number of primary and secondary pumps and all other elements of a vacuum system. Real examples will be used to illustrate accuracy and efficacy.

11:40am **VT-TuM12 Introduction to Molflow+, a New GPU-Based Monte Carlo Code for Simulating Molecular Flows and for Calculating Angular Coefficients in the CUDA Environment*, R. Kersevan***, *J.L. Pons*, European Synchrotron Radiation Facility, France

Molflow+ is a new test-particle (TP) monte carlo (MC) code developed for the simulation of molecular flows. It is the natural evolution of the code Molflow which had been developed by one of the authors (R.K.) and used by many laboratories since 1991. Molflow+ implements modern computing trends, such as the use of the OpenGL graphical interface and C\C++ code, and takes advantage of recent developments in the field of graphical processing units (GPUs) which allow a substantial parallelization of the TP MC algorithm for a modest capital cost. The Compute Unified Device Architecture (CUDA) environment has been chosen for its ease of use and portability to different computing environments. A second version of the program will let a similar code run on computers which have no GPUs or non CUDA-compatible GPUs, and only single or multi-core CPUs. As for the original code Molflow, in Molflow+ the geometry of the vacuum component under study is described in terms of planar polygonal surfaces to which attributes such as transparency, sticking coefficient, desorption profiles and more are assigned. The geometry is defined either by using a built-in editor program or by importing files obtained by using a popular computer-assisted design program which generates a triangularization of the surfaces. A very large period random number generator has been implemented into the code, in order to minimize systematic statistical errors. It will be shown how Molflow+ can also be used to calculate the angular coefficients of arbitrarily complex geometries, which can then be used to perform vacuum calculations based on the resolution of matrix operations. It will also be shown how using the GPU yields a dramatic improvement of the processing speed, thus allowing the simulation of complex vacuum systems which could not hitherto be carried out unless powerful and expensive computing tools were used. The paper will outline the early stages of development of the code, its benchmarking against existing analytical as well as numerical results, and will hint at possible fields of application where the dramatic computational power of the GPU could make a difference as compared to CPU-only cases. It will also discuss possible future developments such as the inclusion of intramolecular collisions which could extend the domain of application to flow regimes other than molecular.

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-TuM

## Exhibitor Workshops
**Moderator:** R. Langley, Consultant

10:00am **EW-TuM1 RFG Vacuum System PC/PLC Controller**, ***C. Malocsay***, Semicore Equipment Inc.

A full featured vacuum sequencer for pump, vent & vacuum interlocking for semi-automated process control. The RFG is a PC based graphical user interface (GUI) with VGA touch screen. Vacuum sequencing and input / output controls are provided by an embedded PLC. The RFG integrates easily with a host of industry proven power supplies, vacuum gauges and deposition instruments.

10:20am **EW-TuM2 New High Performance Vacuum Gauge Controller**, *S. Palmer, B. Langellotti,* ***S. Raczelowski***, Varian, Inc.

Varian's new vacuum gauge controller provides unprecedented capacity, performance and flexibility in a cost effective, standard half-rack package. A single controller can simultaneously operate up to four hot filament (or four cold cathode) gauges and four convection gauges, up to five ionization gauges, or up to twelve convection gauges. Expansion or re-configuration in the field is easy to do. Serial communications (RS-232 or RS-485), eight set points, and universal voltage compatibility are standard in all units. A programmable dot matrix LCD provides display flexibility, and simple screen organization and navigation makes the unit extremely easy to use. Drop down gauge selection automatically sets the emission current, sensitivity and overpressure. The screen displays up to eight gauges and pressures simultaneously, and permits the user to label each gauge. A large-font feature provides visibility from 20 feet.

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-TuL

## Exhibitor Workshops
**Moderator:** R. Langley, Consultant

12:20pm **EW-TuL1 Combining AFM and Instrumented Nanoindentation for Mechanical Characterization of Materials at the Nanoscale***, **A. Bonilla***, Asylum Research

Nanoindentation applications have been a popular technique for characterizing a wide range of materials at the nanoscale. This workshop will discuss the Asylum Research NanoIndenter for true quantitative measurements. Unlike other commercially-available cantilever-based (AFM), the NanoIndenter drives the indenting tip perpendicular to the sample. The force is computed as the product of the spring constant and the measured indenter flexure displacement. This measurement is done by converting the vertical flexure displacement into an optical signal measured at the standard MFP-3D photodetector. Because the two quantities of indentation, depth and force, are computed based on displacements measured with AFM sensors, the indenter has unprecedented resolution. The NanoIndenter is also the first commercially-available instrumented nanoindenter that allows high voltage piezoresponse force microscopy (PFM) measurements. The NanoIndenter can operate, as well, when the sample is heated up to 300° C and under fluid. The technology and operation will be discussed along with current application examples including PFM.

12:40pm **EW-TuL2 Manipulation and Characterization of Nanoobjects in SEM***, **H. Koop***, attocube systems AG, Germany

Ultra-high precision spatial positioning of objects is of prime importance in the emerging field of nanotechnology. attocube systems, a German company located in Munich, manufactures and provides ultra-high precision spatial positioning systems and complete probing tools which are particularly suitable for extreme environmental conditions such as cryogenic temperatures (10 mK – 300 K), high magnetic fields (+31 T) and ultra high vacuum environments (5 x 10-11 mbar). attocube systems' ultra-compact positioning devices enable linear, angular and rotational movement of samples or probes. They are offered in different sizes, as well as materials, and feature an unprecedented variety of applications particularly suitable for extreme environmental conditions. This represents a revolutionary advancement in the field of nano-positioning, leading to new research possibilities in many areas. Applications for these outstanding nanopositioning devices, well-known in many labs around the world, include, amongst other methods, SPM techniques such as confocal microscopy, scanning force microscopy, scanning tunneling microscopy, near-field optical microscopy, and scanning electron microscopy. Due to the unique working principle attocube's nanopositioners are dedicated for usage in challenging application areas where the combination of high accuracy on one hand and large positioning range on the other one is required. Their excellent performance makes them consequently highly suitable for Scanning Electron Microscope (SEM) applications. The necessity of specific SEM tools and equipment for new fields for research and application becomes more important, particularly as the progress on nanofabrication moves the critical dimensions below the optical resolution limit. There is already a wide range of applications available using attocube's SEM tools. One highly sophisticated system is an SEM probe station allowing the manipulation of nanoobjects on sub-nm level as well as the characterization of electrical properties under SEM conditions, simultaneously. The highest level of usability and flexibility offers attocube's new Atomic Force Microscope (AFM) fully integrated into SEM. By combining major advances of these complementary systems, it is possible to run all AFM applications having full visible access to the tip position with respect to sample. For further technical information concerning attocube systems' products, please visit the website www.attocube.com.

1:00pm **EW-TuL3 Momentum Microscope for Angular and Time Resolved Imaging of Valence Band Electron States**, *B. Krömker,* Omicron Nanotechnology GmbH, Germany, *M. Escher,* FOCUS GmbH, Germany, *D. Funnemann,* Omicron Nanotechnology GmbH, Germany, *D. Hartung, H. Engelhard,* Max-Planck-Institut für Mikrostrukturphysik, Germany, ***K. Winkler***, Omicron Nanotechnology GmbH, Germany, *J. Kirschner*, Max-Planck-Institut für Mikrostrukturphysik, Germany

We demonstrate the application of a novel design of a photoelectron microscope in combination with an imaging energy filter for momentum resolved photoelectron detection. We image the complete momentum distribution of photoexcited electron states in an energy plane through the Brillouin zone. The basic concept of the microscope is to project the momentum image from the back focal plane of the objective lens of a Photoelectron Emission Microscope (PEEM) through an energy filter onto an image detector. Our design is based on a PEEM with an imaging energy filter. The spherical ($\alpha^2$) aberrations of the imaging energy filter are strongly reduced by a novel analyzer design. Together with a time resolved imaging detector it is possible to combine spatial, momentum, energy and time resolution of photoelectrons within the same instrument. The time resolution of this type of energy analyzer can be reduced to below 100 ps. The complete ARUPS pattern of a Cu(111) sample excited with He I, is imaged in parallel and energy resolved up to the photoelectron emission horizon (at ±90°). Excited with a Mercury light source (hν = 4.9 eV) the Shockley surface state at the energy threshold is imaged clearly in k-space. With the high transmission and time resolution of this instrument, possible new measurements are discussed: Time and polarization resolved ARUPS measurements, probing changes of bandstructure due to chemical reactions, in-situ thin film growth and investigation of phase transitions e.g. melting or martensitic transformations.

1:20pm **EW-TuL4 Combined Mechanical and Optical Analysis Methods for Surfaces and Coatings***, **J. Powell***, CSM Instruments

In the matter of materials development and device design, the optimization of material properties is instrumental to success of a coating system or surface functionality. CSM Instruments, a company specializing in advanced mechanical surface characterization, offers a wide range of mechanical contact-based testing instruments at the micro- and nano-scale for this purpose. This includes indentation testers for hardness, elastic modulus, creep, and fatigue behavior, tribometers for coefficient of friction and wear measurement, and advanced scratch testing tools for analysis of coating adhesion, scratch resistance, and viscoelastic recovery. To fully characterize a materials' behavior, these tools can be integrated with atomic force (scanning probe) or confocal microscopy to "complete the picture", allowing you to quantify pileup volume and height, indentation depth and width, scratch track width and angle, and spall (chip) size and shape, amongst other deformation features. This presentation will discuss how mechanical and optical tools can be easily combined on a single testing platform. A number of interesting examples from materials research and industrial design centers will also be presented, with explanation of what can be learned from each capability.

## Applied Surface Science
## Room: 207 - Session AS-TuA

## Practical Surface Analysis
## **Moderator:** J. Shallenberger, Evans Analytical Group

1:40pm **AS-TuA1 Practical Surface Analysis : Beyond Acquisition - The Human Factors**, ***I.W. Fletcher***, *S.F. Davies*, Intertek MSG, UK **INVITED**

The development of modern surface analysis equipment over the past few years has changed the lot of the typical surface analyst. Indeed, acquisition of 'world-beating' data is now almost routine for many. Better quality data equates to more reliable and often novel information from analytical work to the benefit of all concerned. Also the 'turnkey' reliability of the modern equipment compared to 'the good old days' means that more time is now available to analysts to concentrate their skills and efforts into research and development, problem solving and customer service issues rather than to fault finding and instrument set-up and tuning. One factor that has remained relatively constant amidst such instrumental development, however, is the human element. Whilst surface analysts and their customers may share a common ancestry they do not always appear to share the same understanding at times. Communication is generally an issue with human nature adding extra dimensions of complication. Bringing money into the equation is also certain not to help matters either. As analysts and service providers, we need to constantly endeavour to ensure that the correct messages get received and understood. This presentation will outline several practical examples using SSIMS and XPS applied to typical 'industrial' samples and problems where the human condition has had an impact.

2:20pm **AS-TuA3 Characterization of Amine Terminated SAMs: What is with this oxygen?**, ***J.E. Baio***, *T. Weidner*, University of Washington, *D.J. Graham*, Asemblon, *L.J. Gamble*, *D.G. Castner*, University of Washington

Self-assembled monolayers (SAMs) of alkanethiols on metal surfaces have been extensively used as model systems. In particular, amine terminated SAMs have been used to model positively charged surfaces. However, unlike simple methyl terminated SAMs, the quality of amine SAMs is harder to control. This difficulty is illustrated by the previously reported x-ray photoelectron spectroscopy (XPS) results from amine terminated SAMs, all of which describe an unusually high concentration of oxygen within the monolayer. Across a range of protocols, the amount of oxygen detected by XPS varies from 5-8 atomic %. There are two hypotheses that could explain the presence of this oxygen. The first is that the SAM is covered with oxygen containing coadsorbates, while the second assumes that the nitrogen, carbon, and sulfur species are oxidizing. To explore these hypotheses, we characterized amine terminated SAMs on gold substrates by XPS, time-of-flight secondary ion mass spectroscopy (ToF-SIMS), and sum-frequency generation (SFG) vibrational spectroscopy. XPS characterization of our amine SAMs yielded oxygen concentrations as low as 2 atomic %. High-resolution XPS results from the S(2p), C(1s) and N(1s) regions did not detect any oxidized species. However, small amounts of oxidized fragments did appear in both the positive and negative secondary ion spectra. Some of the more prominent oxidized fragments detected included $SO_2H$+ and $C_2H_5NO$+ in the positive secondary ion spectra and $SO_3$- in the negative secondary ion spectra. There were two distinct stretches present in the SFG vibrational spectra: one at 3150 cm$^{-1}$ that corresponds to structured water, and a broad peak at 2850 cm$^{-1}$ indicating a high number of gauche defects within the monolayer. Nonetheless, the lack of N-O, S-O, and C-O stretches in the SFG spectra are consistent with the XPS and SIMS results that show oxidation alone cannot completely account for all of the oxygen detected by XPS on the amine SAM surfaces. Therefore, the majority of the oxygen found within these amine SAMs most likely arises from the presence of coadsorbates.

2:40pm **AS-TuA4 XPS Analyses of Patterned Samples: the Particular Case of X-ray Absorbing Compounds or Structures**, *C. Cardinaud*, IMN-CNRS, France, *S. Bouchoule*, LPN-CNRS, France, ***V. Fernandez***, IMN-CNRS, France

Angular X-ray Photoelectron Spectroscopy (XPS) is usually a well suited technique to obtain and discriminate chemical information from the bottom and the sidewall of periodic patterns, such as an array of ridges.[1,2,3] In most commercial XPS systems, the direction of analysis is vertical, i.e. normal to the sample surface, while the x-rays strike the surface with an angle of incidence (α) usually close to the magic angle (54.7°). And the tilt axis is perpendicular to the plane defined by the x-rays and the analyser. Assuming the x-rays are not significantly absorbed by the sample as it is the case for silicon, resists or dielectric materials, this setting allows to analyse the bottom of the pattern (as well as the top of the ridges). Tilting the sample towards the x-ray source to an angle θ, allows to shadow the bottom and observe photoelectrons coming from the ridges sidewall (and the top of the ridges). Obviously the suitable value for θ is given as atan(space width / ridge height). Problems arise whenever the ridges are sufficiently wide to absorb significantly the x-rays. This may occur for III-Vs materials such as InP or GaAs widely used in photonics. For example InP ridges having a width of 1.8µm will absorb 99% of AlKα, under 60° angle of incidence. Then for θ=0 the bottom is irradiated only in part, and very weakly or even not at all if α>atan(space width / ridge height). In the same way, at angle θ to obtain full irradiation of the sidewall that comes in the analyser line of sight requires that θ>α. However this may not be satisfying with regards to the pattern dimension. Taking advantage of the absorption of the x-rays, an alternative angular configuration exists: it consists in tilting the sample opposite to the x-ray source until the bottom is totally screened. Simultaneously, this brings the sidewall that is irradiated in the analyser line of sight. In the present communication we expose and discuss in detail the advantages, drawbacks and limits of these two configurations. The XPS system used here is a Kratos Axis Ultra, several operating modes are experienced for the surface analysis of etched InP patterns.

[1] C.S. Fadley, Prog.Surf.Sci. 16(1984)275

[2] G.S. Oehrlein, J.Appl.Phys. 64(1988)2399

[3] E. Pargon, J.Vac.Sci.Technol. 23(2005)1913.

3:00pm **AS-TuA5 3-Dimensional XPS Imaging of Surface Nano-structures; A New Technique**, ***S. Tougaard***, *S. Hajati*, University of Southern Denmark

XPS energy spectra vary characteristically with the depth distribution of electron emitting atoms on the nano-scale. This is the basis for the by now well known and widely used method[1] to non-destructively determine atomic depth distributions with nano-meter resolution by analysis of the inelastically scattered electrons associated with the XPS peak. A new algorithm which is suitable for automation was suggested recently.[2] For each XPS signal, this algorithm determines the total amount of the corresponding atoms within the outermost ~ 10 nm and it also determines their depth distribution. The validity of the algorithm was demonstrated experimentally by comparison to more elaborate quantification methods.[3] In addition, software that can automatically analyze several thousand spectra corresponding to the situation in XPS imaging is developed. The software produces nondestructively a 3-D image of the surface with nanometer depth resolution. The practical applicability for XPS imaging was recently demonstrated.[4-5] As an example we have demonstrated a quantitative test[4] of the algorithms ability to produce images of Ag taken from a series of samples with increasing thicknesses of plasma patterned Octadiene (2, 4, 6 and 8nm) on Ag substrates. The obtained images of the amount of silver atoms in the outermost few nano-meters of the samples were in good agreement with the nominal thicknesses. For a given sample, different sectioning of depth distributions of atoms were made which clearly prove the ability of the method for quantitative and nondestructive 3-D characterization of nano-structures. In ref [5], 3D images of thermally patterned oxidized silicon made through a photolithographic mask were produced and it was shown that 3-D images of the Si, O, and C atoms were complementary. In the talk we will summarize the technique and discuss its limitations and capabilities.

[1] S. Tougaard Surf. Interf. Anal. 26, 249 (1998)

[2] S. Tougaard, J. Vac. Sci. Technol. A21, 1081 (2003)

[3] S. Tougaard, J. Vac. Sci. Technol. A23, 741 (2005)

[4] S. Hajati, S. Coultas, C Blomfield and S. Tougaard, Surf. Interf. Anal. 40, 688 (2008)

[5] S. Hajati, J. Walton, N. Fairley, and S. Tougaard, Surf. Sci. (2008). In press.

4:00pm **AS-TuA8 Assessment of Computer-assist Automated Peak Identification in XPS (X-ray Photoelectron Spectroscopy)**, ***M. Suzuki***, ULVAC-PHI, Inc., Japan, *S. Fukushima*, *S. Tanuma*, NIMS, Japan

XPS is widely used for the analysis of surface regions to determine elemental composition and chemical state. Peak identification is usually conducted with sophisticated software that is delivered from a manufacturer. In the VAMAS/TWA2/A9 project, we have artificially prepared basic test XPS spectra, corresponding to Au-Ag-Cu ternary alloys with three different compositions, and we also superposed noise onto them. Noise was generated by random number with amplitudes that were numerically defined from total intensity of the basic test spectra.[1] Three basic and noise-superposed spectra were distributed to participants in a round robin test (RRT) to evaluate visual peak detection and peak identification using software in daily use. We will demonstrate peak identification efficiency, referring the results for visual peak detection[2] for the test spectra. We have, first, prepared the reference sets of peak energies and elemental transitions, where we have chosen the peaks with detectabilities more than 75% (9 persons / 12 RRT participants) or with S/N (background-subtracted peak intensity / background deviation at both peak sides) ratios more than 10. The nine persons among twelve RRT participants reported results of automated peak identification for noise-superposed test spectra. 6, 2, and one persons used software of MultiPak (ULVAC-PHI), Casa XPS (Casa Software), and Spectral Data Processor (XPS International), respectively. Analyst A (MultiPak user) showed about 60% of "positive efficiency (PE)" and several % of "negative efficiency (NE)". Here PE means the ratio of the number of identified peaks to that in a set of reference, but NE corresponds to the percentage of peak number not-included in a set of reference. Analyst J (Casa user) reported about 70% PE and 100% NE for the same test spectrum. For one other noisy test spectrum, analysts A and J answered about 60% and 70% PE, and 5-10% and 45-50% NE, respectively. These efficiencies did not depend on the noise amplitudes. The elements assigned by analyst A were only Au, Ag, and Cu, but analyst J reported several other elements. The results evidently prove the difference in design concepts of software. In the presentation, efficiencies depending on software and noise amplitude will be discussed in details.

[1] M. Suzuki, S. Fukushima, and S. Tanuma, J. Surf. Anal. 14, 104 (2007).

[2] M. Suzuki, S. Fukushima, and S. Tanuma, Surf. Interface Anal. Accepted.

### 4:20pm **AS-TuA9 A Novel Bismuth-Manganese Emitter for G-SIMS Spectroscopy and Imaging**, ***F. Kollmer***, ION-TOF GmbH, Germany, *F.M. Green,* National Physical Laboratory, UK, *E. Niehuis,* ION-TOF GmbH, Germany, *I.S. Gilmore, M.P. Seah*, National Physical Laboratory, UK

Static SIMS is a well-established, powerful technique for the analysis of complex molecules on the outermost surface of a solid. However, the complexity of static SIMS spectra and the difficulties in the interpretation thereof have been significant barriers to the wider uptake of the technique. G-SIMS has been demonstrated to be a useful approach for simplifying complex static SIMS spectra of organics at surfaces leading to a direct identification of different substance classes.[1] G-SIMS uses two ion beams that generate high and low fragmentation conditions at the surface. This allows an extrapolation to equivalent experimental conditions with very low fragmentation. The resulting spectra are less complex, contain more structural information and are easier to interpret. A barrier for the wider uptake of G-SIMS into the community are the requirements for two ion beams producing suitably different fragmentation conditions and the need for their registration at the surface, which is especially important for heterogeneous samples. The most popular source is the liquid metal ion source, which is now sold with almost every new ToF-SIMS instrument. These produce a high brightness source of atomic and cluster ions such as $Bi_n^+$, $Au_n^+$. Unfortunately, a preliminary study shows that the cluster primary ions are less suitable for G-SIMS. We have developed a novel emitter consisting of a mixture of bismuth and manganese that produces selectable beams of $Bi^+$ and $Mn^+$ for high and low fragmentation conditions respectively. The beams are automatically aligned at the surface. This combines the cluster beam capabilities of a $Bi_n^+$ cluster source with the ability to give excellent G-SIMS imaging and spectroscopy, without significantly comprising the cluster ion performance. We investigated the fundamental fragmentation conditions of $Bi^+$ and $Mn^+$, their ability to provide clear G-SIMS spectra and compared them to previously applied species as $Ar^+$ and $Cs^+$. Moreover, we investigated the beam performance of the BiMn source and the possibility of high resolution imaging in combination with G-SIMS analysis.

[1] I. S. Gilmore, M. P. Seah, Appl. Surf. Sci. 161 (2000) 465.

### 4:40pm **AS-TuA10 Probing the Polymer-Glass Interface to Understand Adhesion in Laminate Structures**, ***K.M. Stika****, D.G. Swartzfager, D. Huang, R.L. Smith, D.E. Davidson, R.L. Agostinelli, D. Brill*, DuPont

Our ability to optimize and consistently control polymer-glass adhesion is an important property in many glass laminate applications. This poster will review recent rate-dependent peel testing studies that highlight significant differences in adhesion performance between polymer encapsulants and glass surfaces. Coupling quantitative AFM (Atomic Force Microscopy) with XPS (X-ray Photoelectron Spectroscopy) and ToF-SIMS (Time-of-Flight Secondary Ion Mass Spectrometry) analyses of the debonded layers has provided new understanding linking adhesion failure mode with interfacial chemistry.

### 5:00pm **AS-TuA11 Process Qualification and Monitoring of Interconnect Etch Processing using In-Line Total Reflective X-ray Fluorescence Spectroscopy**, ***P.S. Frankwicz****, M. Johnson, T. Budri, T. Moutinho*, National Semiconductor Corporation

Process qualifications and monitoring serve important functions in a high volume semiconductor production environment for insuring process control and product yield. Conventional production qualifications generally involve etch rate, defect characterization and final image critical dimension metrics and generate relatively little quantification of actual etch process excursions in the process chamber. Specifically, elevated levels of chlorine-based residual etch by-productions after interconnect etch can drastically increase the probability of corrosion of conventional Al-Cu (0.5%) metal interconnects. A new multiple parametric qualification (MPQ) has been developed that provides baseline surface composition for interconnect etch and clean process excursion detection using Total Reflective X-ray Fluorescence Spectroscopy (TRXFS). The 180nm technology node qualification includes automatic defect characterization (ADC) and electrically testable metal bridging structures for verification of electrical parametric versus interconnect design rules. TRXFS provides total chlorine content and spatial surface concentration profiling of the qualification wafers to levels of 100ppm range. In this study, total chlorine content after interconnect metal etch and clean has been correlated with high moisture atmosphere exposure tests to determine trigger levels for the start of corrosion of metal interconnect lines via HCl chemical reaction with the aluminum interconnect sidewall. Spatial surface concentrations of chlorine provide wafer maps to detect and investigate process tool variations in wafer backside helium cooling gas, process gas distribution and liquid solvent clean application. The chemical composition results have been correlated with Liquid Phase Ion Chromatograph and Secondary Ion Mass Spectroscopy to verify surface species concentrations. The TRXFS methodology provides definable metrics to compare chamber to chamber process performance and map process space. Furthermore, this surface sensitive protocol can replace cumbersome and time consuming high moisture atmosphere wafer exposure methodologies. Examples of semiconductor production excursions and process improvement investigations will be presented to illustrate the utility of the TRXFS qualification in comparison to conventional production monitoring.

### 5:20pm **AS-TuA12 In-situ ATR-UV Spectroscopy of Adsorption-Desorption Isotherms of Silane on Silica**, ***M.A. Bratescu,*** Nagoya University, Japan, *D.B. Allred,* University of Washington, *N. Saito,* Nagoya University, Japan, *M. Sarikaya,* University of Washington, *O. Takai*, Nagoya University, Japan

Ultraviolet attenuated total reflectance (UV–ATR) spectroscopy is a useful method to monitor electronic transitions of molecules at interfaces via the evanescent wave generated at a totally internally reflecting surface. Silane is a frequently used linker for functionalization and assembly on silica. Many efforts are still made to identify and to optimize the factors affecting the monolayer formation. Reaction conditions such as temperature and humidity, as well as silane and substrate chemistry influence the rate of reaction and the assembly process. We chose a silane based adsorption process to determine what insight this spectroscopic examination may yield. For this study we have used the molecule O-4-methyl-coumarinyl-N-[3-(thriethoxysilyl)propyl] carbamate (Gelest, Inc.), which has the formula $C_{20}H_{29}NO_7Si$, and will be hereafter referred to as MCC-propylsilane. The coumarin group represents the observable chromophore in the UV spectral region, and the silane chemistry is desirable for the functionalization and possibly the assembly on silica.[1] Experiments were performed using a custom-made apparatus,[2] combining a fused quartz internal reflection element as the ATR sensor and a flow cell transparent to the light source. The measuring system was equipped with a chiller to control the interface temperature from -10°C to +60°C with 0.01°C resolution. The MCC-propylsilane concentrations were varied from 0.1 to 5.0 mM. The ATR-UV absorption spectrum of MCC-propylsilane shows two peaks at 270 and 325 nm attributed to pyrone and benzenoid groups, respectively, of the coumarin chromophore. From time-resolved spectra at different MCC-propylsilane concentrations and temperatures the adsorption-desorption isotherms were obtained. The thermodynamic properties are useful for a better understanding of the driving forces of this silane adsorption process.

[1] S.R. Wasserman, Y.T. Tao and G.M. Whitesides, Langmuir 5(1989)1074.

[2] M.A. Bratescu, D.B. Allred, N. Saito, M. Sarikaya and O. Takai, Appl. Surf. Sci.,254(2008)2960.

## 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 generalizeable 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 ($cm^2$) 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 intial 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, $\theta$, 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 $\theta = 5°$ 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, verse 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(Zr0.5Ti0.5)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 alklysilanes 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 epi-fluorescence microscopy with immunostaining, and the results of cell culture studies using these test substrates.

## BioMEMS Topical Conference
## Room: 309 - Session BM+BI+BO+NC-TuA

## 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, multi-variate 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 though 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.

[1] X-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

[2] Functionalized 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

[3] Imaging 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 um-wide by 3000 um-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. Himpsel,* 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 derivates 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 $CF_4$ (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 $O_2$ 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. Tserepi, 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 nanostrucured 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 absorbed 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 frequence (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.

# Electronic Materials and Processing
# Room: 210 - Session EM-TuA

## Complex and Multifunctional Oxides
## **Moderator:** A. Herrera-Gomez, Cinvestav-Unidad Queretaro, Mexico

1:40pm **EM-TuA1 Understanding Metastable Structures in Sputter Deposited Hafnia-Alumina, Hafnia-Zirconia, and Hafnia-Titania Nanolaminates**, ***C.R. Aita***, *E.E. Hoppe, M.C. Cisneros-Morales*, University of Wisconsin-Milwaukee

The formation of metastable nanocrystalline phases during reactive sputter deposition of $HfO_2$-$Al_2O_3$, $HfO_2$-$ZrO_2$, and $HfO_2$-$TiO_2$ nanolaminates on unheated substrates is discussed. In addition to being technologically useful, these nanolaminates are archetypical because their bulk pseudobinary phase diagrams predict three different modes of interfacial mixing: complete immiscibility ($HfO_2$-$Al_2O_3$), complete miscibility ($HfO_2$-$ZrO_2$) and limited miscibility without a common end-member lattice ($HfO_2$-$TiO_2$). Of these individual constituents, all but $Al_2O_3$ (which has structural complexity) form both intralayer and interfacial nanocrystalline phases. However, these are often not bulk equilibrium phases and are termed here metastable. This paper addresses two questions: (1) By what mechanisms do these metastable phases arise? (2) How thermally stable are they at temperatures that a device may see during routine processing? We discuss metastable phases resulting from finite crystal size effects (tetragonal and orthorhombic $HfO_2$ in $HfO_2$-$Al_2O_3$) and heteroepitaxy (tetragonal $Hf_{1-x}Zr_xO_2$ in $HfO_2$-$ZrO_2$). We discuss the formation of a complex interface in $HfO_2$-$TiO_2$ nanolaminates that includes monoclinic $Hf_{1-x}Ti_xO_2$, a metastable phase which here results from a second order phase transition of orthorhombic $HfTiO_2$ (a stable interfacial phase) to accommodate the larger Hf atom at a$HfO_2$-on-$TiO_2$ interface. In all cases, these metastable structures represent self-assembly into the lowest possible energy structures in the absence of long-range diffusion.

2:00pm **EM-TuA2 Band Edge Engineering of Barium Strontium Titanate Thin Films by Ni-doping Driven Changes in Bonding Symmetry of Ti and O**, *H. Seo,* North Carolina State University*, Y.B. Kim,* Hanyang University, Korea, ***G. Lucovsky***, North Carolina State University

Suppression of the transition from direct to trap-assisted Fowler-Nordheim tunneling in metal-insulator-metal (MIM) capacitors is reported when approximately one percent Ni-doped barium strontium titanate (BST) thin film dielectrics are substituted for undoped BST. A significant leakage current reduction and improved breakdown resistance are observed for Ni-doped BST compared to undoped BST. The origin of such a large reliability enhancement of Ni-doped BST was investigated by spectroscopic studies includng spectroscopic ellipsometry (SE) and synchrotron X-ray absorption spectroscopy (XAS) measurements. For Ni-doping at the one percent level, the spectral dependence of the imaginary part of the complex dielectric constant,$\varepsilon_2$, obtained from SE shows significant differences in the band edge trap depth and density relative to undoped BST revealing defect states 0.2 eV shallower in energy and seven-fold reduced in density. This change in the defect state energy in Ni-doped BST is accompanied by a change in symmetry of the Ti atom empty $t_{2g}$ states from either monoclinic/orthorhombic to tetragonal: the two $t_{2g}$ states higher lying in the undoped BST O K1 edge and spectroscopic ellipsomtery $\varepsilon_2$ spectra are merged into to a single state in Ni-doped BST, while preserving the average $t_{2g}$ d-state energy. The physical origin of these changes in the band edge defects is the substitution of divalent $Ni^{2+}$ for tetravalent $Ti^{4+}$ in band edge divacancy defects. Electrical measurements of J-V traces for Ni-doped BST show a symmetric direct tunneling process while undoped BST revealed asymmetric trap assistant tunneling/Fowler-Nordheim conduction process responsible for a rapid current rise. The results on improved Ni-doped BST suggest an approach for BST MIM capacitor in gigabit dynamic random access memory as well as identify a novel band edge state engineering approach based on transition metal doping which should be applied to other oxides with perovskite structures, e.g., $PbTiO_3$ and $PbZrO_3$.

2:20pm **EM-TuA3 Growth and Properties on Multifunctional Epitaxial Oxide Structures**, ***C.H. Ahn***, Yale University **INVITED**

Complex oxides exhibit a wide range of phenomena, including magnetism, ferroelectricity, superconductivity, and colossal magnetoresistance. The epitaxial growth of these complex oxides in crystalline heterostructure form allows these functionalities to be combined and utilized for fundamental science and technical applications. The ability to integrate this class of materials with others, and silicon in particular, multiply these research and technical opportunities. To fully realize this potential, the interfaces between materials must be understood, controlled, and optimized on the atomic level. We have developed techniques for the determination of such interface structures with sub-Angstrom accuracy, and informed by first-principles calculations, we have developed real-space models for complex oxide heteroepitaxy.

4:00pm **EM-TuA8 The Metal-Insulator Transition in Vanadium Dioxide: A View at Bulk and Surface Contributions for Thin Films and the Effect of Annealing**, *W. Yin, K. West, J. Lu,* University of Virginia*, Y. Sun,* Stanford University, *S.A. Wolf*, ***P. Reinke***, University of Virginia

Vanadium dioxide is investigated as potential oxide barrier in spin switches, and undergoes a first order metal-to-insulator (MIT) transition at 340 K, which will provide an actively switchable interlayer as a critical element in the device. In order to incorporate VO2 layers in a complex multi-layer devices it is necessary to understand the relation between bulk and surface/interface properties in order to optimize device performance. Our study focuses on the comparison of the MIT in the bulk and at the surface of thin VO2 layers, and establishes an irreversible modification of the crystallite structure and surface for temperatures exceeding the MIT. The surface modification impacts on the strategies which are employed to build the magnetic contact on a VO2 layer. Highly oriented VO2 thin films were grown on (0001) sapphire single crystal substrates with a novel growth technique called reactive bias target ion beam deposition. In the analysis of the VO2 films we employed bulk-sensitive methods (x-ray diffraction, transport measurements) and surface sensitive techniques (photoelectron spectroscopy, STM). The samples were subjected to a heating cycle with repeated cycling through the MIT, and annealing to at least 100 K above the MIT. The VO2 films exhibit the the transition from the monoclinic to the tetragonal phase, with the concurrent change in conductivity by 10-3. The cycling across the MIT temperature and annealing have no impact on the abruptness and magnitude of the transition, and the bulk-dominated process exhibits therefore the requisite long-term stability. The stability of the surface with respect to annealing is dramatically lower, and electronic and structural changes occur. The observation of the valence band with PES as the film transits through the MIT temperature and the subsequent annealing clearly show that the surface partially retains its high-temperature metallic character. The onset of oxygen depletion at the surface is held responsible for this behavior, and a critical issue in tailoring the interface to the top contact. In addition to the changes on an atomic level, the annealing triggers a rearrangement in the orientation and shape of the crystallites, which is shown in a quantitative analysis of the STM images of the VO2 surface. The in-situ observation of the temperature-induced changes of the surface with STM will provide additional information on the oxygen-depletion and morphological changes in the VO2 surface.

4:20pm **EM-TuA9 Some High k Potential for MIM or RRAM Applications**, ***C. Vallee***, *P. Gonon, E. Gourvest, C. Jorel, M. Mougenot, M. Bonvalot,* CNRS - France, *V. Jousseaume,* CEA/LETI/D2NT - France, *O. Joubert*, CNRS - France

Metal Insulator Metal (MIM) capacitors in silicon analog circuit applications have attracted great attention due to their high conductive electrodes and low parasitic capacitance. Silicon oxide and nitride were commonly used in conventional MIM capacitors. Though they can provide good-voltage linearity and low temperature coefficients, their capacitance density are limited due to their low dielectric permittivity. In order to increase the surface density of MIM capacitors, several technological ways are investigated: realization of capacitors according to 3D architectures and integrating high or medium k materials. First MIM high k investigations dealt with $Ta_2O_5$. Among various high k dielectric materials, medium k such has $HfO_2$, $ZrO_2$ and rare earth oxides should give better performances owing to larger band gap than $Ta_2O_5$ and higher permittivity than silicon nitride. Flash technology is expected to reach its limits by the beginning of the next decade. In this context, existing research efforts are exploring a variety of novel memory concepts including: i) FeRAMs (Ferroelectric RAMs), ii) MRAMs (Magnetic RAMs), iii) PCRAMs (Phase Change RAMs). More recently, the semiconductor research community has shown a growing interest for RRAM (Resistive RAM) which exploits the resistive switching properties of oxides (mainly NiO) to store information. Its main advantages are good compatibility with current CMOS technology, high speed, and low power switching and good temperature stability of the data retention. A PVD process is usually used for the deposition of the oxide. Hence, for both applications (MIM capacitors and RRAM devices) high k dielectrics deposited with a low thermal budget should be a solution. This study is then focused on the deposition and characterization of several high k dielectrics such as $HfO_2$ or $Y_2O_3$ on different metallic electrodes (Pt,TiN,…) for MIM capacitors or RRAM devices. These materials are deposited by ALD or PE-MOCVD processes. The electrical behavior of the structures will be presented and discussed in terms of capacitance density, capacitance linearity and current-voltage characteristics with a special care to the switching mechanism of the high k RRAM. They will be correlated to chemical analysis results (XPS, ATR and FUV-SE), with special attention devoted to metal/oxide interface investigations.

5:00pm **EM-TuA11 Study of Luminescence and Epitaxy of Green Light Emitting ZnO Thin Films Prepared by MOCVD**, ***J.H. Liang***, *Y.J. Chen, J.H. Du, H.Y. Lai*, National Dong Hwa University, Taiwan

ZnO is one of the potential candidates for application on the green light LED, since ZnO has a broad PL peak in the green light region. Since the green light emission is caused by defect level transition in ZnO, epitaxial relationship could affect the behavior of green light emission due to the formation of different types of defects. Therefore, we studied intensively the dependence of luminescence of the ZnO film on the epitaxial relationship between film and substrate in order to get high intensity of green light emission. In our experiment, we prepared ZnO thin films on sapphire substrates by metal organic chemical vapor deposition (MOCVD), using dimethylzinc (DMZn) and oxygen, respectively, as zinc and oxygen source. We changed the Ⅵ-Ⅱ ratios and the growth temperature, and annealed the ZnO thin film at various temperature of 600°C - 1000°C in three kinds of atmospheres (Argon, nitrogen and oxygen). We used XRD to analyze the crystal structure, PL to analyze light emission, FESEM to observe the morphology and TEM to observe the epitaxial relationship between the film and the substrate. We reported the successful growth of dense (002)-oriented ZnO thin films with nearly 100 nm of grain size. We found that the XRD intensity of (002) and the grain size of ZnO grown under all three kinds of atmospheres increase with increasing temperature. We also found that the intensity of UV and green light emission were the highest at 1000°C in oxygen atmosphere, and the improvement of the intensity of green light emission was even more significant. We suggested that the defects of oxygen dominate the intensity of green light emission. We will show the TEM results about epitaxial relation between the film and the substrate to prove that there are 30-degree rotated epitaxial relationship between the film and the substrate. We will discuss about how the epitaxial relationship may affect the green light luminescence.

5:20pm **EM-TuA12 Investigation of Conductive Channel on GaInZnO Surface**, ***J. Lee***, *J. Chung, H.I. Lee, E. Lee, T. Kim, D. Kang,* Samsung Advanced Institute of Technology, Korea, *H.J. Kang*, Chungbuk National University, Korea

GaInZnO (GIZO) is a promising material for oxide thin film transistor which has transparent and high electric mobility. However GIZO has very sensitive to ambient environment. To understand the surface sensitive electrical property of GIZO, the physical properties of GIZO surfaces such as energy band gap, work function, and surface composition were investigated at the GIZO (70nm thick) fabricated by radio frequency sputter deposition on Si(100) and Glass substrate. The energy band gap of GIZO was measured using electron energy loss spectroscopy (EELS) against the energy of primary electron beam. The energy band gap of GIZO (Ga:In:Zn=3:2:1) was increased from 3.0eV to 3.5eV when the energy of primary electron beam increased from 300eV to 2000eV. Because of lower the primary electron beam energy of EELS, more sensitive to of surface, the result says that the energy band gap of surface is about 0.5eV lower than that of bulk of GIZO. When the Ga concentration in the GIZO increased from Ga:In:Zn=2:2:1 to 4:2:1, the energy band gap slightly increased from 3.3eV to 3.6eV. A depth profiling analysis of GIZO by Secondary Ion Mass Spectrometry (SIMS) indicated that GIZO was divided by 4 layers such as Zn+Ga rich, Ga rich, In rich, and balanced GIZO layers. The thickness of altered layer was about 3nm. The concentration of Zn at the surface was higher when the oxygen partial pressure during sputter deposition was higher. The Zn+Ga rich layer was just top monolayer (~0.2nm thickness). The thickness of Ga rich layer was about 0.45nm. The thickness of altered layer of GIZO was well agreement with that of estimated by EELS results. The previous results suggest the existence of a conductive channel on GIZO surface. The characteristics of GIZO based thin film transistor are strongly influenced by the conductive channel which formed near surface. In this report, the existence of conductive channel on GIZO surface will be discussed in detail.

## 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 $Al_2O_3$, 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 (Isc) and open circuit voltage (Voc) 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**

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 ($CuInGaSe_2$, 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 $CuInSe_2$ and $CuGaSe_2$ 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 $CuInSe_2$ 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 electrom 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 $\theta_O$, and that they become semiconductors for $\theta_O \geq 1/2$ with the larger gap at the higher $\theta_O$ (Eg=3.3 eV at $\theta_O=1$). 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 graphne layer of graphite is investigated using scanning tunneling micropscopy 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 occured because of the weak physical interaction between graphen 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 Graphite Oxide (GO) and Graphene Nanostructures**, ***P.E. Sheehan***, *Z. Wei, J.T. Robinson, D.E. Barlow, E.S. Snow*, Naval Research Laboratory

Graphene and graphite 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 solution[3]. 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 $SiO_2$ 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 $CO_2$ 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 $CO_2$ 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.

[1] Stankovich, S. et al. Carbon 45, 1558–1565 (2007).

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

[3] Li, 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 $sp^2$ 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.q. 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 $\pi$ to $\pi^*$ 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.

## IPF 2008 Frontiers in Imaging: from Cosmos to Nano
## Room: 312 - Session IPF-TuA

### Frontiers in Physics
### Moderator: F. Dylla, AIP

2:20pm **IPF-TuA3 Proton Cancer Therapy**, ***J. Flanz***, Massachusetts General Hospital **INVITED**

4:00pm **IPF-TuA8 Optical Atomic Clocks**, ***J. Ye***, National Institute of Science and Technology and University of Colorado **INVITED**

Quantum state engineering of ultracold matter and precise control of optical fields have allowed accurate measurement of light-matter interactions for the development of best atomic clocks. State-of-the-art lasers now maintain optical phase coherence over one second. Optical frequency combs distribute this optical phase coherence across the entire visible and infrared parts of the electromagnetic spectrum, leading to direct visualization and measurement of light ripples. An the same time, ultracold atoms confined in an optical lattice of zero differential a.c. Stark shift between two clock states allow us to minimize quantum decoherence while strengthen the clock signal. For $^{87}$Sr, we achieve a resonance quality factor >2 x $10^{14}$ on the $^1S_0$ – $^3P_0$ doubly forbidden clock transition at 698 nm.[1] The uncertainty of this new clock has reached 1 x $10^{-16}$ and its instability approaches 1 x $10^{-15}$ at 1 s.[2] These developments represent a remarkable convergence of ultracold atoms, laser stabilization, and ultrafast science. Further improvements are still tantalizing, with quantum measurement and precision metrology combining forces to explore the next frontier.

[1] M. M. Boyd, T. Zelevinsky, A. D. Ludlow, S. M. Foreman, S. Blatt, T. Ido, and J. Ye, “Optical atomic coherence at the one second time scale,” Science Vol. 314, pp. 1430 – 1433, 2006.

[2] A. D. Ludlow, T. Zelevinsky, G. K. Campbell, S. Blatt, M. M. Boyd, M. H. de Miranda, M. J. Martin, J. W. Thomsen, S. M. Foreman, J. Ye, T. M. Fortier, J. E. Stalnaker, S. A. Diddams, Y. Le Coq, Z. W. Barber, N. Poli, N. D. Lemke, K. M. Beck, and C. W. Oates, “Evaluation of a Sr lattice clock at 1x10-16 via remote optical comparison with a Ca clock,” Science Vol. 319, pp. 1805 – 1808, 2008.

4:40pm **IPF-TuA10 Diamond Circuitry*, M. Lukin*, Harvard University** **INVITED**

## 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 occured. 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.

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

[2] M. 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 $2 \times 10^7$ erg/cm$^3$ to $2\times10^6$ erg/cm$^3$ as a function of film thickness and Cr concentration. Nanosphere lithography[2] 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. Schift, 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 x 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. Makinen, 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 ~λ/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 colloidally 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 succesful 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.

[1] S.C. Erwin, L. Zu, M.I. Haftel, Al.L. Efros, T.A. Kennedy, and D.J. Norris. Nature 436, 91 (2005).

[2] D.J. Norris, Al.L. Efros, and S.C. Erwin. Science 319, 1776 (2008).

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. Quitoriano, 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 interpaticle 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 pendent 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 ambient[1] and ultra-high vacuum[2] 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 geometry[2]; 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 $\mathrm{Au(111)\text{-}(C_{18}H_{37})_2S}$ 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 stablility 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] Jaegeun 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. Altfeder***, *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 nanocrystaline 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 microcopy (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 Eu3+ 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 Eu3+ 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.

## Plasma Science and Technology
## Room: 304 - Session PS-TuA

## Fundamentals of Plasma-Surface Interactions I
### **Moderator:** K.P. Giapis, California Institute of Technology

1:40pm **PS-TuA1 Examining Sidewall Formation, Passivation, and Etching in Nanometer-Scale Feature Fabrication using Molecular Dynamics Simulation**, ***J.J. Végh***, *D.B. Graves*, University of California, Berkeley

A firm understanding of fundamental etch limitations is becoming increasingly important as the scale down of feature sizes continues in the manufacture of semiconductor and other thin-film devices. Molecular dynamics (MD) simulations have been conducted to model the formation of small (~2-3 nm) features in silicon, both through the use of confined beams of ions and radicals and through exposure of a substrate to ions and radicals through an explicit masking layer. We compare simulations using an amorphous carbon mask on top of the silicon substrate to other simulations assuming a perfectly confined beam of bombarding species (i.e. to mimic a mask) on the same geometry (~2 nm wide trenches). The presence of the masking layer strongly affects the overall etch process and the minimum achievable feature size. For example, material from the mask is seen to sputter into the feature, where it mixes with the substrate material, and subsequently affects the etch yield and chemistry. Likewise, material from the substrate is seen to sputter and redeposit on the sidewalls of the mask, affecting sticking and transport of subsequent incident species. Ion scattering off the walls of the mask also affects the etch process by altering the angle of incidence and energy of the ions that hit the substrate. For certain bombarding chemistries, the masking layer shows severe degradation and loss of structural fidelity. We illustrate how this loss of fidelity in the masking layer transfers to the underlying substrate material on the small scales examined. The role of sidewall passivating radicals vs. the role of ions (i.e. $CF_x$ at 300 K vs. 200 eV $CF_X^+$ ions) is also examined: data on sticking coefficients and scattering probabilities are presented and the relative contributions from ions and radicals to the final sidewall composition are elucidated. Ion bombardment alone is sufficient to form a ~1 nm thick damaged/passivation layer along the sidewall, but deposition from radicals also plays an important role in determining the ultimate sidewall structure as the features deepen. We also discuss the challenges of extending MD to include larger and more realistic systems and other important effects, including substrate charging, long-timescale diffusion, and alternative masking materials such as SiC, etc.

2:00pm **PS-TuA2 What are the Limiting Factors for Etching sub-10nm Si Holes?**, ***Y. Zhang***, *E.M. Sikorski, B.N. To*, IBM Research

Patterning transferring nanometer-scale semiconductor features with precision has pushed us to think of the 'true' limits for plasma etching. One of the possible limits plasma etching facing is what the smallest holes (vertical side wall holes) plasma etching can do. In this paper, we report the recent results of studying plasma etching of nanometer-scale features with a focus on sub-10nm holes into silicon substrates as an examples to study the possible ‘limits’ for pattern transferring by plasma etching. Using diblock copolymer self assembled nanometer-scale patterns as starting templates, we using different methods to shrink the dimensions of the nanometer-scale holes down to sub-10nm regime. We studied plasma etching challenges for etching nanometer-scale holes into silicon with different masks in different plasma chemistries and process conditions. The results indicate that the plasma chemistry, plasma conditions and parameters, substrate temperatures, and the characteristics of aspect ratio dependence all play roles in the etching processes of forming nanometer-scale holes in silicon substrates. Among all the factors, when hole diameters shrinking down to sub-10nm regime, the sidewall passivation formed during the etching of holes with vertical sidewall becomes the determining factor for how small holes can be etched into silicon substrates. The result agrees with the previous studies.[1,2] The impacts of mask materials and selectivity to etch sub-10nm holes will be also discussed.

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[1] Y. Zhang, Plasma Etching of Nanoscale Features, http://meetings.aps.org/link/BAPS.2007.DAMOP.C3.3, Calgary (2007).

[2] J. J. Végh and D. B. Graves, Investigating Fundamental Etch Limits: Molecular Dynamics Simulations of Sub-10 nm Feature Fabrication, AVS 54th International Symposium, http://www2.avs.org/symposium2007/Papers/Paper_PS2-WeM11.html.

2:20pm **PS-TuA3 Investigations of Plasma-Polymer Interactions For Nanoscale Patterning of Materials[1,2]**, ***G.S. Oehrlein***, University of Maryland **INVITED**

The combination of photolithographic patterning of organic materials followed by plasma-based transfer of photoresist patterns into electronic materials enables the production of nanometer scale devices required in information technology products. Despite the success of these thin film and substrate patterning approaches in what is possibly the most important example of nanoscale manufacturing, important gaps in our scientific understanding of relevant plasma-polymer interactions remain. In this talk we will review chemical and morphological changes induced in selected model polymers and advanced photoresist materials as a result of interaction with fluorocarbon/Ar plasmas. Of special interest are the changes of the materials that take place at the beginning of the plasma-polymer interaction period. We will evaluate the respective roles of a) polymer structure/chemistry and b) plasma process parameters on the consequences of the plasma-polymer interactions. The impact of plasma-induced polymer alterations on changes of polymer-defined nanoscale features will also be discussed.

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[1] Based on collaborations with S. Engelmann, R. L. Bruce, F. Weilnboeck, T. Kwon, T.C. Lin, R. Phaneuf, Y. C. Bae, C. Andes, D. Wang, D. Graves, D. Nest, J. Vegh, E. A. Hudson, B. Long, G. Willson, P. Lazzeri, E. Iacob and M. Anderle

[2] We gratefully acknowledge financial support of this work by the National Science Foundation under awards Nos. DMR-0406120, DMR-0705953 and NIRT CTS-0506988.

3:00pm **PS-TuA5 3-Dimensional Monte Carlo Simulation and Experimental Measurements of Surface Roughness under Plasma Etching**, ***W. Guo***, *H. Kawai, H.H. Sawin*, Massachusetts Institute of Technology

Surface roughening on poly-Si, $SiO_2$ and various low-k dielectrics were experimentally measured and modeled in the 3-Dimensional Monte Carlo profile simulator as a function of etching chemistry, ion incidence angle and amount of etching time. Experimental data and modeling results were in good quantitative agreement in terms of etching yield and roughness level, suggesting the incorporated mixing-layer kinetics model is able to accurately account for the chemistry taking place on various substrates and plasma chemistries. Morphologically, all films displayed transverse striation at intermediate ion angle, and parallel striation at grazing ion angle in Ar sputtering or low polymerizing $C_4F_8$/Ar chemistry. The transition from transverse to parallel striation at different ion angles were captured with the profile simulator by combining the curvature-dependent sputtering with surface diffusion suggested by B-H model, through which the impinging ions deliver more energy to the surface in depressions relative to elevations. It was demonstrated experimentally and in modeling that the ripple formation is sensitive to the amount of etching: transverse striation on single-crystal Si at 60°ion angle gave way to parallel striation as etching persisted. The surface roughening mechanism at grazing angle at 75° ion angle was proposed as the micromasking mechanism which effectively roughens the surface with both clean net-etching region and sporadically polymer-rich net-deposition region. The modeled elemental composition was mapped on the surface and compared to the experimental data to disclose the roughening mechanism.

4:00pm **PS-TuA8 Scaling Relationships of Polymer Surface Roughening with Energy Density and Surface Composition during Plasma Processing**, ***S. Engelmann***, *F. Weilnboeck, R.L. Bruce, G.S. Oehrlein,* University of Maryland, College Park, *C. Andes,* Rohm and Haas Electronic Materials, *D.B. Graves, D.G. Nest,* University of California, Berkeley, *E.A. Hudson*, Lam Research

The modifications of 193nm and 248nm PR blanket materials, patterned structures, and model polymers during and after plasma etching were studied using ellipsometry, atomic force microscopy, x-ray photoelectron spectroscopy, and scanning electron microscopy. The plasma parameters examined include bias power, source power and pressure in $C_4F_8$/90% Ar discharges. In addition, $CF_4$/Ar chemistries (0-100% Ar) have been examined. We combined these widely varying plasma conditions in a model addressing the photoresist roughening behavior in oxide etch plasmas. The roughness evolution was based on a transfer mechanism by ions and a characteristic roughening behavior based on the energy density present on the PR surface during processing. We found that in our discharges this roughening behavior scales linearly with the energy density present at the surface during the discharge, suggesting an overriding importance of the molecular structure on the roughening behavior. A proportionality of this scaling based on the molecular structure of the PR material was noted. The resulting surface roughness can be predicted if the polymer structure, exposure time and the energy density during plasma processing are known. We also found that the energy density of the surface could be greatly reduced by an increase in etch yield. The etch yield could be effectively increased depending on the oxygen and fluorine surface coverage of the PR material. Our results indicate that either high removal or high roughening occurs during plasma processing, but both parameters cannot be independently optimized.

4:20pm **PS-TuA9 Plasma VUV-induced Degradation of Polymer Films: Effects of Radiation Wavelength**, ***D.G. Nest***, *T.-Y. Chung, J.J. Vegh, D.B. Graves,* University of California at Berkeley, *S. Engelmann, F. Weilnboeck, R.L. Bruce, T.C. Lin, R. Phaneuf, G.S. Oehrlein,* University of Maryland, College Park, *B. Long, G. Willson,* University of Texas, Austin, *E.A. Hudson*, Lam Research Corp., *C. Andes, D. Wang*, Rohm and Haas Electronic Materials

A fundamental understanding of roughening mechanisms of polymer materials used in pattern transfer during plasma processing is of increasing importance as device dimensions continue to shrink. We have shown that vacuum ultraviolet (VUV) radiation, ion bombardment, and heating all play important roles in the roughening of photoresist materials. In this study, we further investigate the role of VUV radiation in the degradation of polymer materials. Exposure to VUV radiation results primarily in the loss of carbon-oxygen bonds in the bulk of PMMA-based polymers, such as 193-nm photoresists. However, the VUV spectrum impacting the substrate depends on the processing conditions and especially on the gas composition. In a vacuum beam apparatus, we exposed PMMA-based photoresist to VUV radiation from various gases using a remote inductively coupled plasma. The radiation from the source was calibrated spectrally. The range of VUV radiation wavelengths responsible for polymer degradation was isolated using various VUV transparent windows and implications for polymer processing are discussed.

4:40pm **PS-TuA10 Plasma Radiation Effects on Photoresist Degradation and Depth Fluorination of Photoresists in Fluorocarbon Discharges**, ***F. Weilnboeck***, *S. Engelmann, R.L. Bruce, G.S. Oehrlein,* University of Maryland, *D.G. Nest, D.B. Graves,* University of California, Berkeley, *C. Andes, D. Wang,* Rohm and Haas Electronic Materials, *E.A. Hudson*, Lam Research Corp.

The influence of radiation generated by Ar and Ar/$C_4F_8$ plasmas on the material degradation of photoresists (PR) is studied. Blanket films of fully formulated 193nm and 248nm PR were exposed to different radiation spectra, ranging from visible to vacuum ultraviolet light. Radiation was filtered by placing the PR underneath a structure containing transparent windows with different cut-off wavelengths, i.e. borosilicate glass (310nm) or $MgF_2$ (120nm). Thickness changes, chemical and morphological evolution of the PR surface were characterized using Ellipsometry, Atomic Force Microscopy (AFM), X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared Spectroscopy (FTIR). It was found that 193nm PR is highly sensitive to radiation wavelengths between 120nm and 310nm while 248nm PR was unaffected. The evolution of surface roughness and bulk material modifications with time was also analyzed by AFM and FTIR, and will be reported. Furthermore, we investigated the effect of bulk fluorination in 193nm and 248nm PR materials. Previous observations point towards material dependent differences of fluorination depth in the bulk for materials exposed to fluorocarbon plasmas. This phenomenon is poorly understood and will be addressed by exposing the PR materials to a $C_4F_8$/90%Ar discharge followed by depth profiling. Results will be presented at the meeting.

5:00pm **PS-TuA11 Ar Ion Sputtering of GaAs Studied by Molecular Dynamics Simulation and Laser Spectroscopy of Ga Atoms in the Gas Phase**, ***E. Despiau-Pujo****, *P. Chabert*, LPTP, CNRS - Ecole Polytechnique, France, *R. Ramos, G. Cunge, N. Sadeghi*, LTM, CNRS - UJF - INPG, France

III-V compounds such as GaAs or GaN-based materials are increasingly important for their use in optoelectronic applications, especially in the telecommunications industry. Photonic devices including lasers, photodetectors or LEDs, require reliable dry etching processes characterized by high etch rate, profile control and low damage. Recently, inductively coupled plasma-reactive ion etching (ICP-RIE) has been used to etch GaAs and its alloys.[1] Due to its high plasma density, ICP-RIE generally results in a high ion flux with moderate ion energies. However, ion bombardment during the etching process can damage the material and lead to amorphisation at high doses. Molecular dynamics (MD) simulations of GaAs sputtering under low-energy Ar ion bombardment were recently developed by Despiau-Pujo et al.[2] This study showed that a significant fraction of Ga products leave the surface with more than 10% of the incident ion energy. The aim of the present work is to verify the simulation predictions and measure the velocity distribution function of Ga sputtered atoms. We describe the operation of a GaN laser diode at 403.3 nm for the spectroscopy of Ga atoms in an ICP argon discharge. To obtain both perpendicular and longitudinal velocity components, LIF measurements are performed in z direction and atomic absorption spectroscopy in x direction. Ga atoms are sputtered from the wafer surface by energetic ions produced in the Ar buffer gas of an industrial ICP etch reactor (LAM 9400). The external cavity diode laser is tested and tuned on resonance with Ga transition. For various pressure and ion energy conditions, we perform a systematic study of the Doppler-broadened LIF and absorption spectra to extract perpendicular and longitudinal velocity distributions of sputtered Ga atoms. At very low pressure, these distributions are compared to sputtering theory and MD results. We observe a good agreement between MD predictions and experiment, even if simulations tend to overestimate the perpendicular velocities of sputtered atoms. These results confirm the existence of products sputtered from the surface with significant energies, which constitutes a key point since these atoms could alter passivation layers on sidewalls during etching, and be responsible for defects observed in nanodevices.

[1] Y. Matsukura et al, J. Vac. Sci. Technol. B 18, 864 (2000)

[2] E. Despiau-Pujo et al, J. Vac. Sci. Technol. A 26, 274 (2008).

5:20pm **PS-TuA12 Modeling of InP Etching under High Density Plasma of $Cl_2$/Ar**, *B. Liu*, ***A. Rhallabi***, *J.P. Landesman*, Institut des Materiaux Jean Rouxel, France, *J.L. Leclercq*, Institut des Nanotechnologies de Lyon, France

It is now evident that the improvement of the optical and electrical performances of the III-V components depends on the optimization of the critical process steps such as the dry etch processes especially for the submicron devices. The simulation of plasma surface interaction may widely contribute to the optimization of such process type. In the present study, a gas phase kinetic model of Cl2/Ar plasma combined to surface model is developed to predict the etching profiles as a function of the plasma parameters. The gas phase kinetic model is based on the mass balance equations of reactive species. The kinetic constants of electron impact reactions are established as a function of electron temperature assuming maxwellian distribution of electron energy. The additional equation of power balance in the ICP reactor allows to determine the electron temperature evolution with the plasma discharge parameters (Rf power, reactor pressure and the chlorine flow rate). Parametric studies concerning the effects of the plasma parameters like power, pressure and percentage of Cl2 on the transport of charged and neutral specie evolutions have been carried out. On the other hand, the simulation results show that electron density and the dissociation rate of Cl2 are more sensitive to the surface recombination coefficient of atomic chlorine. The later is estimated at 0.15. Langmuir probe is used to measure the electrical parameters of Cl2/Ar plasma mixture such as, electron temperature and density as a function of the plasma discharge parameters. A satisfactory agreements between the simulations and the experiments have been observed One of the advantage of our model is the coupling between the plasma chemistry model and the surface etching model. The later is based on the Monte-Carlo approach which allows to describe, in a probabilistic manner, the surface mechanisms for InP etching . The direct fluxes of the reactive species such as Ar+, Cl2+, Cl+ and Cl are determined from the gas phase kinetic model and introduced as the input parameters in the InP etching model. The simulation results show the role of different plasma parameters on the etched surface profiles.

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* PSTD Coburn-Winters Student Award Finalist

## Advanced Surface Engineering
## Room: 204 - Session SE-TuA

## Photocatalytic Coatings
**Moderator:** P.H. Mayrhofer, Montanuniversität Leoben, Austria

2:40pm **SE-TuA4 Wettability Controlled Surface of Photocatalytic Coatings : Application for Dynamic hydrophoboicity**, ***T. Watanabe***, *N. Yoshida*, The University of Tokyo, Japan **INVITED**

Highly hydrophobic coating attracts much attention for long time as antifouling surface because it provides low energy surface whose interaction with contamination is smaller. Especially hydrophobic coating with photocatalytic oxidation capability is expected to become an ideal antifouling surface. According to Young, Dupre and Girifalco-Good equations, substances that can be highly hydrophobic are restricted to polymer material. Therefore it is usually hard to obtain highly hydrophobic thin film with TiO2 photocatalyst because polymer material is oxidized by photocatalysis. Moreover TiO2 photocatalyst itself is hydrophilicized by photo illumination. Due to such reasons, there are not many reports of hydrophobic coating with photocatalyst. However the situation can be dramatically changed when the concept of dynamic hydrophobicity is introduced. Parameter of dynamic hydrophobicity such like sliding speed or sliding angle does not depend on not only thermodynamic stable parameters but it strongly depends on surface microstructure. In fact, we have been investigating the dynamic hydrophobicity on self-assembled monolayer surfaces and found that the dynamic hydrophobicity is strongly affected by the surface roughness of only a few nanometers. Therefore if we focus on dynamic hydrophobicity, the inorganic substances can become potential candidates for having higher hydrophobicity by controlling surface roughness. Inorganic materials are hardly oxidized by TiO2 photocatalysis, and this is a great advantage. Of course even though a high flat surface is obtained, a water droplet cannot form on the surface and the liquid does not slide off as a droplet. Therefore, we have to choose an inorganic material with the lowest possible hydrophilicity. Although most of the inorganic materials exhibit a higher surface energy as compared to organic materials, it was reported that HfO2 is less hydrophilic. Therefore, we have prepared HfO2 combined with a TiO2 composite film and examined the water sliding angle of the surface. The result shows that the surface processed by the optimized preparation procedure shows a water contact angle of around 70° and a sliding angle of 30° are observed. This surface also shows high photocatalytic decomposability against IPA. Also very recently, we have obtained TiO2 with highly dynamic hydrophobic surface by physical deposition process. It shows sliding angle of 17 ° and at the same time show fairly well photocatalytic activity.

4:00pm **SE-TuA8 The Role of Carbon in Anatase as Visible Light Photocatalyst**, ***Y.J. Chen***, *G.Y. Jhan, M.S. Wong*, National Dong Hwa University, Taiwan

Titania is known as the favorable material as photocatalyst. However, the wide bandgap of titania limits its efficient utilization of solar light with most photon energies below the bandgap of titania. In this paper, we report that titania powders synthesized by low-pressure flat-flame metalorganic chemical vapor deposition shows high photocatalytic efficiency under visible light illumination. Using acetylene and oxygen as fuel and oxidizer for the flame, the titanium isopropoxide was decomposed and oxidized, and the nanoparticles of titania were formed. The phase of titania powder can be manipulated by carrier gas flow rate such that the higher the carrier gas flow, the higher the rutile content. From the methylene blue decomposition study we found that the powder with almost pure anatase phase synthesized under slightly oxygen deficient environment possesses best photocatalytic efficiency under illumination of visible light. The reaction rate constant is even higher than that of ST-01 titania powder, which is commercially available for photocatalytic applications. The visible light absorption is resort to the presence of carbon since no other chemical bonds not associated with carbon are chromophores. It also suggest that carbon species are associated with catalytic site on anatase surface so that carriers generated by photon absorption by the carbon species can transfer quickly onto catalytic sites and perform the subsequent catalytic reactions. Evidence will be provided to show that the carbon species does evolve with annealing, and the presence of carbon species is in coincident with the presence of visible light absorption.

4:20pm **SE-TuA9 Nb-doped $TiO_2$ Thin Films for Solar Energy Conversion**, ***P.A. DeSario***, *K.A. Gray, M.E. Graham*, Northwestern University

A deeper understanding of synthesis, structure and function is needed to improve the design of materials tailored to solar energy conversion and storage. This study highlights the efficacy of reactive sputtering as a means to fabricate cation-doped $TiO_2$ films having controlled properties tailored to the generation of energy rich fuels such as $CH_4$ or $CH_3OH$ by photoreduction of $CO_2$. It is our hypothesis that cation substitution in the $TiO_2$ lattice is an effective way to shift the photoresponse of the material further into the visible light region without deleteriously modifying its photochemical properties. Unbalanced reactive dc magnetron sputtering (UBMS) with partial pressure control of oxygen was utilized to synthesize a series of pure and mixed phase $TiO_2$ films. Films were doped with Nb to evaluate the effect of cation doping on optical, chemical and physical properties. Nb doping was achieved by altering a pure Ti target in a pieced manner by adding slugs of dopant material at regular intervals. The films were interrogated structurally and functionally using SEM, EDS, XPS, XRD and UV-vis spectroscopy. The ability of these materials to selectively and efficiently reduce $CO_2$ to energy rich fuels was evaluated in a gas phase reactor coupled with a GC/FID. While earlier work established the relationships between sputtering process parameters and the film structure, including phase identity and distribution in pure $TiO_2$[1], this work is focused on how the addition of Nb cations in the range of 0-20%Nb change the film growth and phase formation relative to the pure material. The work also tries to characterize the cation valence and location in the $TiO_2$ lattice, but this is still under investigation. The parametric response of film structure still suggests that in the mixed phase system, greater energy input favors the formation of rutile and lower energy favors anatase, but the Nb additions shift the regions of phase stability compared to the pure $TiO_2$ case. The shift in optical absorption to the visible wavelength range as a function of Nb concentration and anatase-rutile phase distribution is also presented.

[1] L. Chen, et al., Fabricating Highly Active Mixed Phase $TiO_2$ Photocatalysts by Reactive DC Magnetron Sputter Deposition. Thin Solid Films, 2006. 515(3): p. 1176-1181.

4:40pm **SE-TuA10 Effect of Phase, Crystallinity and Carbon Content on Photocatalysis of Carbon-Doped Titania Films**, *P.W. Chou, Y.S. Wang, **M.S. Wong***, National Dong Hwa University, Taiwan

Amorphous pure and carbon-doped titania films were prepared by reactive sputtering of titanium metal target and co-sputtering of Ti and carbon targets, respectively, in Ar and oxygen plasma. The as-deposited films were subsequently annealed in vacuum and in air. The influence of annealing atmosphere and temperature on the composition, phase and crystallinity of the films was systematically studied to understand their effects on photocatalytic activity. Both the pure and the carbon-doped films annealed in air transformed into anatase phase at 300℃ and retained pure anatase phase even at 800℃; while those annealed in vacuum transformed into rutile/anatase mixed phase at 300℃ and into pure rutile at 600℃. Carbon incorporation and oxygen deficient environment seem to favor phase transformation of amorphous titania to rutile at low temperatures in post-annealing.

5:00pm **SE-TuA11 Rules for Efficient Titania Coatings. Applications to Water, Air and Material Cleaning**, ***J.-M. Herrmann***, CNRS-Université de Lyon, France **INVITED**

Photocatalysis concerns Fine, Green and Environmental Chemistry. Titania coatings must follow the rules of photocatalysis with the influence of 5 basic parameters governing the activity (mass of catalyst, wavelength, concentrations or partial pressure of reactants, temperature and radiant flux). Besides mild selective oxidations obtained by generating active neutral atomic O* species in the absence of water, photocatalysis can detoxify inorganics in water by oxidizing them in their harmless upper oxidized state. Similarly, organic pollutants are totally oxidized in CO2. Complex molecules (pesticides, dyes, herbicides, insecticides) are totally destroyed as well as bacteriae (E.Coli, streptococcus faecalis) in water without re-growth. Air pollutants (VOC's, odors) can also be destroyed by cracking OH° radicals produced by UV-irradiated titania-coated supports. The applications concern domestic anti-odor refrigerators, electronics with a "molecular" purity of the ambient working atmosphere, the destruction of odors emitted by water treatment plants and solid waste landfills. Eventually, Virus H5N2, a model virus close to H5N1, responsible for the aviar flu, was totally destroyed in a contaminated air flux of 40 $m^3$/h with a 99.93% efficiency in a single pass. Photocatalytic self-cleaning technology consists in depositing sub-micronic thin layers of titania at the surface of glass, metals, concrete, etc, whose photocatalytic activities are calibrated by test-reactions. In the real world, dirty materials, such as glasses, to be "self-cleaned" are soiled by greasy and sticky deposits, which, in addition, induce a strong adherence of ambient dusts. The mechanism of self-cleaning glasses was elucidated by the mineralization of palmitic acid ($n\text{-}C_{15}H_{31}\text{-}COOH$), present in the human sebum and in the natural varnish of plants. It disappeared by successive "photo-Kolbe" reactions with photo-produced holes $h^+$. The linear hydrophobic aliphatic chains are progressively "peeled off," carbon atom after carbon atom, via successive photo-Kolbe reactions. Palmitic acid degradation would require 16 of them. Fortunately, the overall self-cleaning glass process can be strongly accelerated by by-passing many intermediates via the release of several VOC's in the atmosphere, quite innocuous for the environment. The efficiency of titania demands two requirements: (i) a good cristallinity (anatase phase) and (ii) a high (cationic) purity.

## 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 $NH_{3,ad}$ 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 ($N_{ad}$ + $N_{ad}$ and $N_{ad}$ + $O_{ad}$). At low oxygen coverages ($\theta_O < 0.5$ ML), adsorbed ammonia is stripped to $NH_{x,ad}$ 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 ($CO_3 = CO_2 + O_a$) 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 CeO2(111)) and the inverse model catalysts (CeOx or TiOx nanoparticles supported on Au(111) or Cu(111)) have significant intrinsic activity for water-gas shift at elevated pressures. Neither Au(111) nor CeO2(111) have any activity in the WGS reaction. Our photoemission data indicate that CeOx nanoparticles supported on the gold surface dissociate water molecules even below room temperature while the CeO2 nanoparticles are inactive. Water dissociates on O vacancies of the oxide nanoparticle (the

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* Morton S. Traum Award Finalist

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 O2 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 TiOx 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 eneretics of dissociative adsorption of O2 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 TiO2 fragments (modeling a substrate). For all missing row n+0.5 Au structures under consideration, the total energy is found to decrease upon the O2 dissociative adsorption. However, analysis of entire pathway for this reaction suggests that the O2 dissociative adsorption is favorable only for 1.5Au/TiO2 structure. This result along with the experimental finding[1] point to the O2 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.

[1] M. 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 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 **SS1+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 $CO_2$ conversion and hydrogen separation. An understanding of the nature of $H_2$-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 $H_2$ 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 **SS1+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. Rubinovich***, *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" (FCEM[1]), 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. Rubinovich, Surf. Sci. Rep. 38 (2000) 127.

[2] M. Polak and L. Rubinovich, Phys. Rev. B 71 (2005) 125426.

[3] M. Polak and L. Rubinovich, Phys. Rev. B 75 (2007) 045415.

5:00pm **SS1+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 $Au_2O_3$ 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 AuFe[5] and Pt nanoclusters deposited on $TiO_2$(110) will be presented.

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

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

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

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

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

5:20pm **SS1+NC-TuA12 The Morphology and Reactivity of Metallic Nano Clusters Deposited on $SiO_2$ 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 $SiO_2$/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 $2106\pm2cm^{-1}$. 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.

## Surface Science
## Room: 209 - Session SS2-TuA

## Dynamics and Novel Probes
**Moderator:** M.G. White, Brookhaven National Laboratory and State University of New York at Stony Brook

1:40pm **SS2-TuA1 Excited Electrons in Interfacial Chemistry**, ***A.M. Wodtke**, I. Rahinov, R. Cooper,* University of California, Santa Barbara, *D.J. Auerbach*, GRT Inc. **INVITED**

Developing a predictive understanding of surface reactivity incorporating the possible breakdown of the Born-Oppenheimer approximation represents one of the most important challenges to current research in chemical dynamics. Furthermore, to the extent that Born-Oppenheimer breaks down, we have no predictive theory of surface chemistry. This means we are working in an exciting environment where new phenomena might be discovered through experiments and inspire new theoretical developments. This lecture will present recent experimental results from our group that bears on this topic. For example, when molecules with low levels of vibrational excitation collide with metal surfaces, vibrational coupling to electron-hole pairs is not found to be strong unless incidence energies are high. However, there is accumulating evidence that coupling of large amplitude molecular vibration to metallic-electron degrees-of-freedom can be strong and becomes more important at reduced incidence translational energies. This can occur due to charge transfer between the surface and the molecule and the high kinetic energies associated with bond compression/formation. These conditions found in these experiments simulate reaching a chemical transition-state also and we are intrigued to pose the basic question: are electronically non-adiabatic couplings important at transition-states of reactions at metal surfaces? This implies theoretical approaches relying on the Born-Oppenheimer approximation may not accurately reflect the nature of transition-state traversal in reactions at metal surfaces. In related work, we have been looking at the energy transfer processes between molecules and surfaces that enable molecular trapping, the first elementary step in “Langmuir-Hinshelwood” reactions. We find remarkably large amounts of translational energy can be channeled to a metal surface and are able to look at this for different quantum-state to state scattering channels. While our results require additional theoretical comparisons, it appears that phonon coupling may not be sufficient to explain these experimental observations.

2:20pm **SS2-TuA3 Chemicurrent Measurements using Alkali Metal Covered Pd/p-Si(001) Schottky Diodes**, ***D. Krix**, K. Huba, H. Nienhaus*, University of Duisburg-Essen, Germany

Non-adiabatic energy dissipation, e.g. the creation of electron-hole pairs, plays an important role in the understanding of chemical reactions at metal surfaces. For a large number of gas-metal reactions it is possible to measure hot charge carriers produced while exposing the metal to reactive gases as chemicurrents. The method is based on depositing thin metal films on a semiconducting substrate in order to form a rectifying electrical device - i.e. Schottky diodes. Hot electrons and holes may be ballistically injected into the semiconductor for energies larger than the intrinsic barrier at the interface. Thermalising in the bulk of the semiconductor the current can not flow back into the metal other than through the measuring circuit. Therefore large area, nanometer thick Pd films were grown on wet chemically prepared, hydrogen terminated, Boron doped p-Si(001) substrates. The palladium diodes are used as a platform for further deposition of alkali metal layers. Palladium was chosen for its low barrier height ( 0.38 eV ) on p-doped silicon, making the diodes most sensitive to low energetic hot holes while retaining excellent device characteristics. This barrier is also considerably lower than that of pure alkali-Si diodes – 0.58 eV for potassium. Chemicurrent, Auger spectroscopy, as well as Kelvin probe data are presented for the adsorption of molecular oxygen and molecular hydrogen on Pd and K/Pd surfaces at low temperatures ( T = 120 K). During the oxidation with molecular oxygen the chemicurrents show as at least two distinct maxima. Varying the initial alkali coverage changes the relative contribution of the maxima to the chemicurrent. The overall charge detected increases monotonically with potassium coverage. After the deposition of about two monolayers of potassium a saturation is seen of about $1\mu As/cm^2$. Increasing the Pd film thickness results in a strong exponential attenuation of the observed charge. This is strong support for the identification of the detected currents as due to hot hole generation at the surface. The data give an estimate of the probability to generate a hot hole in a reaction event of approximately 1%.

2:40pm **SS2-TuA4 The Role of Surface Atom Motion in Methane Activation on Ni(111)**, ***V.L. Campbell***, Tufts University, *D.R. Killelea,* University of Chicago, *N. Chen, A.L. Utz*, Tufts University

Quantum state resolved gas-surface reactivity measurements have yielded detailed insights into how a gas phase reagent's vibrational energy promotes reaction, but our understanding of how surface vibrations influence reactivity is less complete. Here, we show that state-selected reagents, with their precisely defined internal and translational energy, are powerful probes of the reaction dynamics along other important energetic degrees of freedom, including surface atom motion. We focus on how surface atom motion influences the distribution of energetic barriers experienced by methane molecules prepared in v=1, J=2 of the $\nu_3$ C-H stretching state and incident on a clean Ni(111) surface. Recent theoretical work suggests when a nickel atom is displaced above the (111) surface plane, the energetic barrier for reaction decreases. Within a dynamical framework, this result suggests that increasing surface temperature increases the probability that an incident methane molecule will impact on a Ni atom in this energetically favorable geometry. Statistical models of reactivity assume that energy in phonon modes is pooled to activate the reaction complex; increased surface temperature increases the pool of energy available to activate the reaction. We use state-selected reagents, with their well-defined internal and translational energies, to quantify reaction probability as a function of incident kinetic energy at a series of surface temperatures. At each surface temperature, the state-resolved reaction probability curves we obtain reveal the effective distribution of barriers along the translational energy coordinate. Changes in the shape of the effective barrier height distribution function with respect to surface temperature reveal how surface atom motion impacts reaction energetics. Our ability to prepare and control the non-equilibrium distribution of energy among the many degrees of freedom in this system permits a test of the energy pooling assumption.

3:00pm **SS2-TuA5 Low-Temperature Growth of Si/Si(111)-(7x7) by Femtosecond Pulsed Laser Deposition**, ***I.A. El-Kholy***, *H. Elsayed-Ali*, Old Dominion University

Surface morphology during the growth of Si on Si(111)-(7x7) by femtosecond pulsed laser deposition (fsPLD) is studied using reflection high-energy electron diffraction (RHEED) at different temperatures. The growth of Si on Si(111) has received considerable attention as a model system of homoepitaxy. PLD is a deposition technique that uses much more energetic species (atoms and ions) compared to other physical vapor deposition (PVD), such as in molecular beam epitaxy. In PLD, the deposition process consists of periodic bursts of laser-generated plume followed by uninterrupted surface relaxation. This periodic nature of deposition differs from other PVD methods, and this could affect the growth mechanism. The use of ultrafast lasers vaporizes the target rather than melting it, thus minimizes the formation of particulates. In this work, in situ RHEED was used to study the dynamics of PLD of Si on Si(111)-(7×7). A Ti-sapphire laser (100-fs, 800-nm, 1 kHz) was used to ablate the Si target to generate a plume that deposite on a Si(111)-(7x7) kept at varying temperatures. The experiment was performed in an ultrahigh vacuum chamber at a residual gas pressure of $5x10^{-9}$ torr. It is observed that the decay of the RHEED pattern during deposition is due to the increase in the surface roughness. Epitaxial growth of Si/Si(111)-(7x7) at temperatures as low as 350°C was observed. For this substrate temperature, no change in RHEED patterns was observed after growth, with only reduction in intensity during deposition. This indicates that the growth mechanism was step-flow.

4:00pm **SS2-TuA8 Scanning Near Field Infrared Microsocopy (SNIM) – Combining Topographical and Chemical Mapping of Bio Materials**, ***M. Havenith***, Ruhr University Bochum, Germany **INVITED**

We have set-up a scanning near field microscope (SNIM) in Bochum. As radiation source serves an Infrared Opto Parametric Oscillator (IR-OPO) and a CO laser. This allows us to cover the chemically important frequency range of the amide bands and the C-H and O-H stretching region. In 2007 our group has reported chemical imaging of microstructure self-assembled monolayers (SAMs) with nanometre resolution[1] using SNIM. This study demonstrated the extreme sensitivity of SNIM which even allowed recording the IR spectrum of a single monolayer of a specific absorbing functional group (biotin). Our measurements were carried out on a microcontact printed line pattern of a monomolecular film of biotinylated alkylthiolates. Whereas in conventional IR microscopy, about 1 µm thick layers of protein sample are required in order to record a full IR spectrum, here the IR fingerprint spectrum of approximately 30 000 biotin molecules in a 90 nm by 90nm patch of 3.7 nm height were detected. Biotin can also be considered as a model system for more complex protein systems. Further applications include the use for label-free analysis of biochips on the nano-scale. The possibility of simultaneously accessing topographic and spectroscopic information from biological nanostructures could be the basis for a new generation of nanodevices e.g. for medical diagnostics. As a proof-of-principle we demonstrate the feasibility of detecting hybridization reactions in nanostructured DNA-patches. For the DNA nanofabrication process we use nanografting which is a scanning probe microscopy based lithography technique. The nanografted single stranded nano structures can be clearly detected within the double stranded self assembled monolayers due to their distinct IR frequency response. Moreover, even nanografted double stranded nanostructures can be imaged since they have a higher packing density, yielding increased IR absorption in the corresponding amide band. This work is carried out in cooperation with the group of L. Casalis and G. Scoles at ELETTRA.

[1] I. Kopf, J.-S. Samson, G. Wollny, Ch. Grunwald, E. Bründermann, and M. Havenith, Chemical imaging of microstructured self-assembled monolayers (SAMs) with subwavelength resolution, J. Phys. Chem. C, 111 (23), 8166-8171 (2007).

4:40pm **SS2-TuA10 Non Statistical Patterns of Chemical Reactivity on Metals**, ***A.L. Utz***, *D.R. Killelea*, Tufts University

Facile electron- and phonon-mediated energy exchange channels on metal surfaces have the potential to support rapid and extensive energy exchange during a reactive collision, but recent state-resolved reactivity measurements of methane's dissociative chemisorption on Ni have produced clear evidence for incomplete (non-statistical) energy redistribution prior to reaction. Examples include vibrational-mode selective chemistry (in which reactivity is influenced not only by the amount of vibrational energy available, but also by the identity of the excited vibrational state), the observation that vibrational and translational energy differ in their ability to activate reaction, and even bond-selective chemistry (selective excitation of the C-H stretch in $CHD_3$ prior to surface impact increased the C-H : C-D bond cleavage ratio among products nearly 100-fold relative to an isoenergetic ensemble of $CHD_3$ whose vibrations were statistically populated). We will describe a mechanistic framework for understanding the origin of observed non-statistical reactivity and predicting the propensity for such behavior in other systems. The model builds on numerous experimental and theoretical studies of intramolecular vibrational energy flow and quenching in the gas phase, in liquids, and at surfaces, and it focuses on the timescales for key energy exchange processes relative to reaction. It provides a qualitative explanation for observed reactivity patterns, intuitive guidance for understanding and predicting reactivity patterns, and it and identifies attractive targets for future experimental and theoretical work to better understand and exploit these effects.

5:00pm **SS2-TuA11 Adsorption versus Interaction Strength: Analysis of Molecule-Surface Interactions of Organic Molecules on Pt and Pt-Sn Surfaces with HREELS and DFT**, ***J. Haubrich***, University of Bonn, Germany, *D. Loffreda, F. Delbecq, Y. Jugnet, P. Sautet,* Ecole Normale Supérieure de Lyon, France, *C. Becker, K. Wandelt*, University of Bonn, Germany

Studies on catalysis such as the selective hydrogenation of α,β -unsaturated aldehydes on transition metal surfaces represent a challenge to both experimentalists and theoreticians. In order to elucidate the underlying elementary reactions, the assignment of the adsorption structures of complex molecules on model-catalyst surfaces is a fundamental step. Insight into the molecule-surface bonding of these structures is crucial for instance to understand the different hydrogenation activities and selectivities of multifunctional molecules on various catalysts. Furthermore introducing alloying effects to catalyst surfaces can change the properties of catalysts significantly and, thereby give rise to additional modifications of the molecule-surface interaction. Here we present a complementary experimental and theoretical study on the molecule-surface interaction of different organic molecules including ethene, butadiene and the α,β-unsaturated aldehydes crotonaldehyde and prenal on Pt(111) and two ordered Pt-Sn surface alloys. With the combination of HREELS (high-resolution electron energy loss spectroscopy) experiments carried out on the three model-catalysts and complimentary density-functional theory (DFT) calculations of vibrational spectra, we identified the stable adsorption structures on Pt(111) as well as the Pt2Sn/Pt(111) and the Pt3Sn/Pt(111) surface alloys. Surprisingly, we find that the changes in the vibrational shifts for corresponding structures on the three surfaces induced by the alloying cannot be satisfactorily correlated with the changes in the adsorption energies. However, with a detailed energetic analysis of the molecule-surface bonding, new insights on the interaction strength with the substrate are obtained that allow to rationalize the behavior of the vibrational properties.

5:20pm **SS2-TuA12 Examination of Force Interactions on Surfaces with Atomic Resolution Using Noncontact Atomic Force Microscopy**, ***T.C. Schwendemann***, *B.J. Albers, M.Z. Baykara, N. Pilet, E.I. Altman, U.D. Schwarz*, Yale University

Interaction forces on the atomic scale govern the underlying physics of many fields of nanotechnology research, such as, catalysis, thin film growth, device fabrication, and tribology. Therefore, we present a method of atomic force microscopy which allows for the generation of 3D force maps of sample surfaces with atomic scale resolution. A homebuilt tuning fork based noncontact atomic force microscope (NC-AFM) facilitates the measurement of tip position and frequency shift that can be translated into force. Until recently, acquisition of surface forces on the atomic scale has been restricted to low resolution maps of single point force curves or 2D atomic resolution (xz) maps. The main difficulty in producing 3D force maps has been minimizing the drift of the instrument over the long acquisition times associated with 3D data collection. To address this issue, our low temperature ultrahigh vacuum NC-AFM was built with a high degree of thermal and mechanical stability. This stability has been demonstrated by our first 3D measurements on highly oriented pyrolytic graphite (HOPG). We chose HOPG as a test material in order to investigate the atomic scale origins of its qualities as a solid lubricant. Data was collected spanning several unit cells laterally and vertically from the attractive region to where no force interactions could be measured. A fine data mesh shows pN forces with less than 7 pm lateral and 1-2 pm vertical resolution. From this 3D data set, cuts along any plane can be plotted in 2D. Cuts in a plane parallel to the sample surface show atomic resolution. Cuts along the surface normal visualize how the atomic attractive force fields extend into vacuum. Now that this technique has been demonstrated it may serve for the further study of chemical force interactions. It is our intention to apply this technique to simple metal oxide surfaces to determine the chemical force interactions between the scanning probe tip and specific surface sites.

# Synchrotron-based Spectroscopy and Spectro-Microscopy Topical Conference
## Room: 310 - Session SY+SS+BI-TuA

## Synchrotron-based Spectroscopy and Spectro-Microscopy
## **Moderator:** Ch. Wöll, Ruhr-University, Germany

1:40pm **SY+SS+BI-TuA1 Ultrafast Surface Dynamics in the Light of Soft X-rays from Free-Electron Lasers: First Results and Perspectives,** ***W. Wurth***, University of Hamburg, Germany **INVITED**

To investigate ultrafast electron dynamics and atomic motion in real-time is essential for a fundamental understanding of complex wave packet evolution in materials. As ideal tools for this type of investigation one can envision time-resolved spectroscopic techniques in the XUV or soft x-ray regime using femtosecond pulses. Tools such as angle-resolved photoemission (ARPES), electron spectroscopy for chemical analysis (ESCA), x-ray absorption or emission spectroscopy have proven to be extremely useful to study the electronic structure of complex materials in a static mode. Powerful XUV or soft x-ray sources delivering ultrashort pulses will enable us to obtain element-specific information on dynamic changes in the local electronic structure. With the Free-Electron Laser in Hamburg (FLASH) a unique source for femtosecond XUV-pulses with unprecedented brightness is operational since 2005 and a number of pioneering experiments have been performed with this source during the first user runs. In the talk I will review some of these experiments and present some ideas how femtosecond x-ray pulses from free-electron lasers can be used to study dynamic processes at surfaces and interfaces. I will show first examples for time-resolved experiments performed at FLASH including the investigation of XUV induced changes in optical reflectivity[1] as well as time-resolved photoelectron spectroscopy[2] and discuss implications for future experiments.

[1] C. Gahl et al., Nature Photonics 2, 165 (2008)

[2] A. Pietzsch et al., New Journal of Physics 10, 033004 (2008).

2:20pm **SY+SS+BI-TuA3 Soft X-ray Spectromicroscopy of Protein and Peptide Interactions with Polymer Surfaces,** ***A.P. Hitchcock***, *B.O. Leung, J.L. Brash, R. Cornelius,* McMaster University, Canada, *A. Scholl, A. Doran*, Lawrence Berkeley National Laboratory **INVITED**

The biocompatibility of a material is dependent on its surface characteristics and how they affect the protein layer which forms upon initial contact with blood or tissue since those proteins mediate subsequent cellular responses. Chemical, mechanical and spatial characteristics are known to play a role in controlling initial protein adsorption. Thus direct measurements of adsorption preferences on structured biomaterials are highly relevant to optimization of biocompatibility. We are using synchrotron based X-ray PhotoEmission Electron Microscopy (X-PEEM) and Scanning Transmission X-ray Microscopy (STXM) to study preferential adsorption of proteins (human serum albumin (HSA), fibrinogen (Fg)) and peptides (sub-6, a cationic antimicrobial) to several phase segregated polymer blend surfaces – PS/PMMA[1,2] and PS/PLA. The X-ray absorption contrast is sufficient to identify and quantify the polymer and protein/peptide components, and peptides can be differentiated from proteins.[3] Single or competitive adsorption is carried out under controlled concentrations, pH, buffer, temperature and exposure times. All of these factors affect adsorption. Image sequences measured in the C 1s, N 1s and O 1s regions are analyzed by pixel-by-pixel spectral fitting to reference spectra. The resulting component maps are placed on quantitative thickness scales, either intrinsically in STXM (when reference spectra are provided on quantitative linear absorbance scales), or by normalizing total signal to a 10 nm measured sampling depth in PEEM. For adsorption on PS/PMMA, under all conditions there is a strong preference to adsorb at the domain interphases, which are thermodynamically favored since both hydrophobic and hydrophilic interactions can be satisfied. Otherwise, HSA and Fg have a preference for PS over PMMA. When sub-6 and HSA are co-adsorbed at neutral pH, there is evidence that the site distribution is controlled by preferential adsorption of a solution complex.[4] Under basic conditions (pH=11) this complex is unstable and the preferential adsorption becomes similar to that seen when each component is adsorbed independently.

[1] C. Morin et al., J Electron Spec, 137 (2004) 785.

[2] L. Li et al., J Phys Chem B 110 (2006) 16763, ibid, 112 (2008) 2150

[3] J. Stewart-Ornstein et al., J. Phys. Chem. B 111 (2007) 7691

[4] B.O. Leung et al., Biointerphases 2008, submitted.

3:00pm **SY+SS+BI-TuA5 Advances in Scanning Transmission X-Ray Microscopy: Surface Sensitive Electron Spectromicroscopy,** ***B.M. Haines***, University of Saskatchewan, Canada, *T. Tyliszczak*, Lawrence Berkeley National Laboratory, *S. Beyhan, S.G. Urquhart*, University of Saskatchewan, Canada

Scanning transmission x-ray microscopy (STXM) is a powerful technique that allows for near edge x-ray absorption spectroscopy (NEXAFS) and imaging with chemical speciation at spatial resolutions better than 50 nm. STXM has seen widespread use to study polymers, biological systems, and geochemistry. Many synchrotrons now have at least one beamline dedicated to STXM. It is however a bulk technique with limited surface sensitivity, as such it is not ideal for studying surface phenomenon or monolayers such as Langmuir-Blodgett films where the signal is very weak. Recently we have modified STXM microscopes at the Canadian Light Source and the Advanced Light Source to perform total electron yield (TEY) NEXAFS, which is well suited for studying surface phenomena. We have used TEY-STXM for compositional mapping of phase separated Langmuir-Blodgett films of arachidic acid and perfluorotetradecanoic acid. The films are imaged with the same resolution as STXM with increased contrast and surface sensitivity. TEY-STXM has been used to obtain simultaneous transmission and TEY spectra in addition to compositional maps of $Fe_3O_4$ carbon supported nanoparticles less than 75 nm in size. The modification of STXM for TEY detection represents a significant new tool for studies conducted with STXM and opens the window for surface sensitive measurements with STXM.

4:00pm **SY+SS+BI-TuA8 Recent Advances in Material Research with Synchrotron Infrared Spectromicroscopy at Elettra,** ***A. Perucchi***, Sincrotrone Trieste, Italy, *S. Lupi,* CNR-INFM Coherentia and Universita' di Roma "La Sapienza", Italy, *D. Eichert, L. Vaccari, M. Kiskinova*, Sincrotrone Trieste, Italy **INVITED**

The infrared beamline SISSI (Source for Imaging and Spectroscopic Studies in the Infrared) at Elettra extracts the infrared and visible components of synchrotron emission for applications of spectroscopy, microspectroscopy and imaging. The applications cover a wide range of research fields, including surface and material science, biochemistry, forensics, geology, biomedicine, microfluidics. We will overview the characteristics of the beamline and discuss recent results. A particular focus will be devoted to the new research opportunities in infrared spectroscopy at high pressures and in the THz range.

4:40pm **SY+SS+BI-TuA10 The Brightest Light Downunder,** ***R. Lamb***, University of Melbourne and Australian Synchrotron **INVITED**

The Australian Synchrotron, a 3 GeV Instrument located in Melbourne, is the newest facility of its type in the world and is poised to become the single largest scientific and technological user facility in the Southern hemisphere. This talk will outline some if the key aspects of the local Science driving the future developments of the facility. An example of work in the area of nanoscale wetting of surfaces will also be described. Synchrotron small angle x-ray scattering (SAXS) has been used to investigate the in situ immersive wetting of ultrarough surfaces which exhibit superhydrophobicity with extreme water contact angle ($\theta$=169). Reduced scattering contrast observed from rough surfaces when partially or totally wetted reveals significant physical differences between superhydrophobic surfaces not otherwise apparent from conventional contact angle measurements. As a complementary technique to static and dynamic contact angle measurements, transmission SAXS-based immersive wetting measurements promise more predictive models for how complex heterogeneous morphologies affect the phenomenon of wetting.

5:20pm **SY+SS+BI-TuA12 Digital In-Line Soft X-ray Holography as Microscopy Technique for Biological Samples,** ***A. Rosenhahn***, *R. Barth, F. Staier, C. Christoffis,* University of Heidelberg, Germany, *T. Simpson, S. Mittler,* The University of Western Ontario, Canada, *S. Eisebitt,* BESSY, Berlin, Germany, *M. Grunze*, University of Heidelberg, Germany

Digital in-line soft X-ray holography (DIXH) is used as lenseless microscopy technique to investigate biological samples. The experimental setup follows directly the initial idea of Gabor,[1] a holographic projection microscope based on a diverging photon beam. By creating a large divergence and the use of short wavelength, a lateral resolution better than 400 nm can be achieved without using any optical elements such as zone plates. Objects composed of different materials and thickness are used to determine the imaging properties of holographic microscopy in the VUV and soft X-ray wavelength range.[2] By tuning the x-ray energy to core resonances, element specific contrast can be obtained.[3] These results are promising with respect to the possibility to exploit intrinsic contrast mechanisms for biological samples. Using fibroblasts and other cells, the sensitivity of the technique to resolve small structures inside these extended objects will be discussed. Although the spatial resolution still needs to be improved, we consider these experiments as starting point for future lensless holospectroscopy and as microscopy approach for highly coherent x-ray sources such as free electron lasers.

[1] D. Gabor, Nature 1948, 161, 777

[2] A. Rosenhahn, R. Barth, X. Cao, M. Schürmann, M. Grunze, S. Eisebitt, Ultramicroscopy 2007, 107, 1171

[3] A. Rosenhahn, R. Barth, F. Staier, T. Simpson, S. Mittler, S. Eisebitt, M. Grunze, Journal of the Optical Society of America A 2008, 25(2), 416.

## 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 ($Al_2O_3$, $HfO_2$ and $La_2O_3$) 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 Formamidinate 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 ºC 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 inexpensive because of their natural abundance. In this presentation, we report the Y, Yb and Er precursors based on formamidinate 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.

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

[2] International 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.

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

2:40pm **TF-TuA4 Electrical Properties of Plasma-Enhanced Atomic Layer Deposition $HfO_2/HfO_xN_y/HfO_2$ 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) $HfO_2$ gate oxides with nitrided middle layer ($HfO_2/HfO_xN_y/HfO_2$) 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 $HfO_2$ 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 $LaAlO_3$ 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 ($LaAlO_3$) films were deposited on hydrogen-terminated silicon substrates by atomic layer deposition (ALD) at 300 ºC. Capacitance-voltage measurements made from ALD MoN/$LaAlO_3$/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 ($O_2$) exposure either after each ALD cycle or by a post-deposition $O_2$ treatment at 300 ºC, without affecting the dielectric constant ($\kappa$~15). The $O_2$ 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 ºC) or low carrier concentration ($<10^{18}$ $cm^{-3}$) 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 $SiO_2$ with a gap of 1 mm. Conductance was measured in situ during initial nucleation and steady state film growth at temperatures between 100-140 ºC. The growth rate, electrical resistance, surface morphology, and crystallininty were also studied ex situ as a function of growth temperature and ALD cycles. At 120 ºC the growth rate of ZnO ALD on $SiO_2$/Si was ~1.9 Å/cycles with ~3 cycles of incubation time and linear with the number of cycles. At 120 ºC 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 ºC, 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. Ritala,*** *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 flaws[1] 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 strenghtening 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/$H_2O$ and SAM24/$O_3$ 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 $mm^2$ to 1200x1200 $mm^2$. Typical film thicknesses were in the range of 10-30 nm, but thicker coatings were also evaluated. Batches of smaller pieces (20x50 - 100x100 $mm^2$) 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 $SiO_2$-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 $SiO_2$ 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 $1070^oC$. 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. $NH_3$ 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.

## Vacuum Technology
## Room: 205 - Session VT-TuA

## Vacuum Gauging and Calibration
### **Moderator:** J. Setina, Institute of Metals and Technology

1:40pm **VT-TuA1 Pirani Vacuum Gauge for J-PARC 3GeV Synchrotron Vacuum System*, M. Kuroiwa*,** *S. Fujii, N. Matsumoto, M. Sasaki,* Tokyo Electronics Co., Ltd., Japan, *N. Ogiwara, Y. Hikichi*, Japan Atomic Energy Agency

Turbomolecular pumps (TMPs) are used for not only rough pumping but also evacuation during beam operation. The backing pressure of the TMPs is always monitored with Pirani gauges. The control unit for the gauge has been newly designed, as the unit should be placed far from the gauge head which is located in a high level of radiation and electrical noise. We have adopted the combination of the constant current method with four-point probe method. Thus, with these techniques the output has been confirmed experimentally to be independent of the cable length, and less influenced by the noise. Generally the constant current method is not so suitable for measuring the higher pressure than that with constant temperature method, because the change in the output voltage so drastically decreases increasing the pressure over than about 100 Pa. As we have to measure the pressure up to about 1000 Pa precisely in order to monitor the backing pressure of TMPs, we have carried out the experiment about the change in the output as a function of the current. And, we have confirmed that the higher pressure can be measured when the higher current is passed. For example, we can measure the pressure less than 20 Pa at 50 mA, and the pressure ranging from 20 Pa to 1000 Pa at 90 mA, respectively. Thus the current is controlled in such a way that the set value is increased with the increasing pressure in several stages. On the other hand, to minimize radiation exposure during maintenance, it is necessary for the gauge head to have high toughness against the vibration and abrupt air inlet etc. Thus we tried to use W wire as the filament instead of Pt wire. However W wire would be unstable characteristic in high temperature status (over the 300C). It had might be affected by oxidation. So we have investigated other material for the filament. Now we have got good data by using W wire with gold coating 30 micrometer in a diameter. 30mA, 10ohm. Still we continue to have investigation to get more toughness and good condition for filament.

2:00pm **VT-TuA2 Hot Cathode Ionization Gauge Life Extension in the mTorr range by Operational Modifications*, P.C. Arnold*,** Brooks Automation, Inc.

Improvement of hot cathode ionization vacuum gauge lifetime in the mTorr range by reducing the sputtering of gauge electrodes onto other components of the gauge will be demonstrated. Of special interest with respect to the sputtering are deposits on the cathodes and on the feedthrough insulators which result in impaired electron emission and leakage currents, both ultimately causing gauge failure. Analytical procedures which led to the sources of the sputtered material will be described. The sputtering reduction is accomplished by reducing the potential difference through which ions are accelerated, consequently reducing the impact energy on low potential electrodes and thus reducing the yield of the sputtering. Empirical data results will be shown to agree with theory and calculations. Other changes in gauge operation to implement these modifications and other improvements to enhance high pressure gauge life will be discussed.

2:20pm **VT-TuA3 Vacuum Metrology in Korea, Value Innovation for Customers*, K.H. Chung*,** Korea Research Institute of Standards and Science (KRISS) **INVITED**

The Korea Research Institute of Standards and Science (KRISS) is the National Metrology Institute of Korea and responsible for the establishment, maintenance and dissemination of the national measurement standards. The Vacuum Technology Center (VTC) in KRISS has maintained the vacuum and leak standards from the atmospheric pressure down to 5x10$^{-7}$ Pa. The vacuum standards systems for low, high, and ultra-high vacuum have been developed. Through bilateral comparisons with NIST, PTB, NMIJ, NPL (UK), IMGC and CCM key comparison for CCM.P-K3 and CCM.P-K4, it is recognized that the KRISS vacuum standards have reached the top level. In an effort to apply the vacuum and leak standards, VTC drew up and carried out the project “Base Construction for Vacuum Technology” from the year 1999 to 2007. The goal of the project was to establish the center in which almost all kinds of vacuum parts, devices, and equipments can be evaluated and performance tested. Its purpose is to help vacuum industries by providing them technical data needed in their development of vacuum equipments or processes. The next step for VTC is to develop the methods to diagnosis plasma processes in reaction chambers and precursor level and contaminations for advanced vacuum processes like semiconductor and display fabrication.

3:00pm **VT-TuA5 Investigations of Gas Dynamics in Capacitance Diaphragm Gauges*, M. Wüest,*** INFICON Ltd, Balzers, Liechtenstein*, V. Kolobov, A. Vasenkov*, CFD Research Corporation

Industrial vacuum processes such as chemical vapor deposition (CVD) can affect the long-term stability of vacuum gauges. This sensor drift can be caused by deposition of process by-products on the surfaces of the sensor. Here, we present chemically reactive gas dynamics inside capacitance diaphragm gauges (CDG) in a CVD process. We present modeling results for the formation and deposition of process by-products in gauges with different geometries.

4:00pm **VT-TuA8 NIST Experience with New Non-Rotating Force Balanced Piston Gauges for Low Pressure Metrology*, J.H. Hendricks*,** National Institute of Standards and Technology

The NIST Low Pressure Manometry Project maintains and operates primary standard ultrasonic interferometer manometers (UIMs) over the pressure range 0.01 Pa (vacuum) to 360 kPa (3.6 times atmospheric pressure). The typical gauging technologies used to cover this important pressure range have included high-accuracy capacitance diaphragm gauges (CDG), resonance silicon gauges (RSG), piezoresistive transducers (PZT), and piston gauges (PG). Over the past 6 years, a new type of customer gauge, the non-rotating force-balanced piston gauge or FPG, has been compared to the NIST 140 Pa UIM and 160 kPa mercury UIMs. The results of these customer comparisons will be presented along with the advantages and disadvantages of using this new high-accuracy device to both generate and measure pressures between 1 Pa and 15 kPa.

4:20pm **VT-TuA9 UHV Gauges in Theory and Practice*, M.L. Stutzman,*** Jefferson Lab*, B.R.F. Kendall*, Elvac Laboratories

Many factors affect the measurement of pressure in the ultra-high vacuum regime. The operating theory of the various hot filament and cold-cathode gauges will be briefly reviewed, followed by a more in-depth discussion about the factors that affect the different gauges. Operational behavior and stability of both hot filament gauges, such as the Bayard-Alpert, Modulated BA and Extractor gauges, and cold-cathode gauges, particularly the inverted magnetron gauge, will be addressed.

4:40pm **VT-TuA10 A New Static Expansion System for the Spanish Metrology Center (CEM)***, N. Medina, S. Ruiz,* Spanish Metrology Center (CEM)***, J. Gómez-Goñi***, Universidad Politécnica de Madrid, Spain

The Spanish Metrology Center, in cooperation with the Technical University of Madrid (UPM) is developing a static expansion system to be used as pressure primary standard in the range from 0,0001 Pa up to 1000 Pa. This standard will be used to calibrate capacitance diaphragm gauges and spinning rotor gauges. The system consists of five vessels: two 100 L-vessels, two 1 L-vessels and one 0,5 L-vessel. It also has two 300 L/s turbopumps (for N2) in order to evacuate the system. The system has been designed to be bakable up to 150 C in order to facilitate its degasification. The system is also endowed with 16 Pt100 temperature probes in order to measure the temperature distribution on the vessels. As auxiliary pressure gauges it also has one mass spectrometer, two ionization gauges, two spinning rotor gauges and two capacitance diaphragm gauges. The expansion factor determination is performed by gas accumulation method. The use of a Ruska 2465 pressure balance and a DHi FPG8601 pressure balance connected to the system through a 1 Torr differential capacitive diaphragm gauge is a special feature of this expansion factor determination. In this way we expect to reduce our measurement uncertainties.

5:00pm **VT-TuA11 Precision Volume Measurements: Challenges to Reducing Uncertainties*, S.M. Thornberg*,** *J.M. Hochrein, J.R. Brown, R.D. Boyd*, Sandia National Laboratories

In order to reduce uncertainties in gas law calculations, one must address each of the major variables: pressure, temperature and volume. Very accurate temperature and pressure gauges are available and can be measured directly with commercial instruments. However, volume is typically the variable in the ideal gas law that consistently contributes greatly to the uncertainty when performing gas calculations. Reducing the volume uncertainty is particularly challenging because volume is not measured directly but is derived from other dimensional, pressure, volume, mass and/or temperature parameters. A delta-V/delta P method for accurately measuring volumes will be presented along with a discussion of ways used to reduce uncertainties and randomness. This method uses calibrated micrometers and precision pressure gauges in an “isothermal” (the goal is to reach a thermal stability where the temperature drifts less than 0.001°C during the 15 minute measurement duration) environment, all of which provides measurement repeatabilities within +/- 0.005 cc for a nominal 10 cc volume.

5:20pm **VT-TuA12 Thermal Management of Temperature Controlled Capacitive Diaphragm Gauges*, B. Andreaus*,** *H. Hanselmann, M. Wüest, Ch. Berg*, Inficon AG, Liechtenstein

We present results from our thermal management studies for INFICON’s new, innovative family of SKY digital capacitive diaphragm vacuum gauges which covers a temperature range from controlled 45°C to hot 200°C as well as full-scales from 1000 Torr to 100 mTorr. A wide range of interface configurations is made possible by a flexible gauge power and communication interface platform. The heart of the design is a new programmable heater architecture that surrounds the high precision ceramic measurement cell and as well controls the temperature gradient between the gauge and the flange. Much thought has been put into heat distribution, material choice and mechanical design in order to achieve a compact and robust design that will provide stable measuring conditions while keeping electronics and software protected and functional in hostile process environments. We present results from our thermal management design studies, complemented by relevant performance characteristics of the gauges from validation experiments.

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-TuA

## Exhibitor Workshops
**Moderator:** R. Langley, Consultant

3:20pm **EW-TuA1 Deposition Tolerant Langmuir Probe**, *D. Gahan, B. Dolinaj,* ***M.B. Hopkins***, Impedans Ltd.

In a standard Langmuir probe system the monitoring of plasma parameters during plasma deposition is limited by the effects of probe surface contamination. A number of issues arise: i) A Langmuir probe immersed in the plasma during deposition processes is subjected to the deposition of a layer resulting in a large disturbance of the probe characteristic. Surface contamination changes the work function, resulting in a shift of the probe characteristic and/or in hysteresis in the I-V Characteristic. The formation of dielectric layers causes the slope of the characteristic to become shallow and eventually reduce the current to zero. This problem is addressed in current Langmuir probe systems based on electron or ion cleaning but limits the probe operation to plasma with low deposition rates. ii) A poor ground return path for the electron current causes shifts in the plasma potential. While this problem is addressed in modern probe systems by using a floating reference probe to compensate for low frequency effects, in deposition plasmas the reference electrode cannot be cleaned by electron bombardment and may be become insulating. The poor electron ground return is made worse by insulating coatings on the wall. In order to produce a Langmuir probe that can operate well in deposition plasma we have introduced a high frequency swept probe. The probe attains a dc bias negative relative to the plasma potential and draws a net current close to zero. The probe records the ac IV characteristic or complex impedance of the sheath and determines the plasma parameters. This technique is valid even in the case of a fully insulating layer forming on the probe surface. The probe draws little net current and minimal ground return is required. We show that the plasma to ground sheath capacitance provides sufficient current during the electron collection period. A unique feature of the probe is the ability to attain a bias voltage above the plasma potential even when coated with a non-conducting layer. We show results of the system in an O2/N2 plasma and compare the swept probe with a standard Langmuir probe.

3:40pm **EW-TuA2 Latest Developments and Application of the Qtac100 for High Sensitivity LEIS**, ***N. Havercroft***, ION-TOF USA, Inc., *E. Niehuis, T. Grehl*, ION-TOF GmbH, Germany

The new high sensitivity and high resolution Low Energy Ion Scattering (LEIS) instrument, the Qtac$^3$, delivers quantitative top atomic layer characterization. It is able to quantitatively analyze the outermost atomic layer of a solid and gain in-depth information in a non-destructive way. The surface is bombarded with low energy (up to 8 keV) noble gas ions that scatter from individual surface atoms. The energy of the ions after scattering is characteristic of the mass of the surface atom. If the scattering event occurs below the surface, an additional depth dependent energy loss can be measured, providing information about the composition of the sample up to 10 nm deep ("static depth profiling"). With its unique energy analyzer, the scattered ions are detected with high sensitivity, while simultaneous high mass resolution allows unambiguous elemental identification. With a pulsed ion beam and time-of-flight filtering, the background of sputtered ions can be resolved from the scattered ions, improving the detection limits for light elements and for trace element detection. Together, this allows an application of the Qtac to many technologically relevant fields. We will present the latest developments of the Qtac100, and show the benefit of the instrument to a variety of applications from traditional surface science to industrial uses. Among these, semiconductor materials (e.g. thin films, layer growth) and heterogeneous catalysts (e.g. Au/Pt nano-clusters, determination of poisoning sites) are the most prominent ones, but other fields that require quantitative top atomic layer characterization will also be addressed.

## Applied Surface Science
## Room: Hall D - Session AS-TuP

### Aspects of Surface Analysis Poster Session

**AS-TuP1 UNIFIT 2008 - Spectrum Processing, Analysis and Presentation Software for Photoelectron Spectra**, ***R. Hesse***, *P. Streubel, R. Denecke*, University of Leipzig, Germany

The aim of the development of the program UNIFIT is to combine appropriate description of the spectra by adequate models, convenient data handling, and excellent numerical performance for fast calculation with versatile opportunities for data transfer, comfortable handling, extensive graphical design options and fast export of high resolution graphics. The advantage of the presented software is the complete treatment of the data from the measurement up to the presentation. (i) The three commonly applied models for fitting photoelectron spectra: product, sum, and convolution of Gaussian and Lorentzian functions will be discussed. In order to illustrate the differences of the models a Cu 3p spectrum was fitted with two independent single lines and an adjustable background consisting of a 3rd degree polynomial and a Shirley background. The theoretically expected intensity ratio of $3p_{3/2}/3p_{1/2}$ of 2:1 is well reproduced applying the sum or (correct) convolution model but not with the product function. (ii) The study of the band structure of solids demands the knowledge of valence-band edge and Fermi level position. We recommend improved methods for determination of these values. (iii) The reliability of the quantification from XPS data was improved using calibrated intensity scales of the photoelectron spectrometer ESCALAB 220 iXL. Two different sub-routines for estimating the transmission functions T(E) of different acquisition modes of any photoelectron spectrometers are integrated in the software UNIFIT 2008. (iv) The new software offers nine different presentations: measured and fitted spectrum, transmission function, Wagner plot, 3D-waterfall 0°, 3D-waterfall 45°, 3D-waterfall -45°, 3D-colour profile, 3D-presentation of fitted spectra and parameter plot. Extensive graphical design tools permit the individual creation of the presentations. The graphics may be exported as BMP or JPG images with a resolution of 600 dpi. The saved pictures may be easily inserted in each Power Point presentation or Word document. (v) The batch-processing submenu serves as a fast and comfortable treatment of parameter-dependent experimental series, e.g., depth profiles, angle resolved spectra etc. (vi) UNIFIT permits the calculation of fit parameter errors after peak fitting. According to the chosen option the user can calculate the errors with two different methods: matrix inversion or iterative calculation.

**AS-TuP2 Test of the Consistency of Angle Resolved XPS Data for Depth Profile Reconstruction Using the Maximum Entropy Method**, *A.J. Roberts, K Macak*, ***D.J. Surman***, Kratos Analytical Ltd, UK

Angle resolved XPS is a useful method for obtaining non-destructive quantification of thin (4-6nm) layers with good absolute depth resolution.[1] Although acquisition of ARXPS data with modern instrumentation is easy, determining the depth distribution of elements from the data is more challenging. The maximum entropy method (MEM) is a technique frequently used for solving the inversion problem in angle resolved XPS experiments. The MEMSYS algorithm used by Livesey and Smith[2] can provide an estimate of the optimum value of the regularising parameter (smoothness), of the error bars in the reconstructed profile and of the noise level in the experimental data set. While for the artificial ARXPS datasets the interpretation of these factors is straightforward, the fitting of the experimental data may be complicated by the sample structure which does not always agree with the assumptions postulated by the model used in MEM calculations : the electron transport in the sample must be determined by the inelastic scattering with the constant mean free path throughout the sample and the material density must be constant throughout the sample. The necessary condition for the consistency of experimentally measured data with the MEM model (successful fit) is that the Laplace transform of the compositional depth profile (LTCDP) calculated from the experimentally measured normalised intensity is a monotonically decreasing function for all measured elements. We have found an efficient algorithm which can estimate the LTCDP for elements with different inelastic mean free paths and thus provide an independent estimate of the noise scaling calculated by the MEMSYS algorithm and verify whether the MEM model is appropriate for the measured data. Here we present results from a number of samples and draw conclusions on the use of these methods to generate elemental and chemical-state depth profiles.

[1] P.J. Cumpson, J. Electron Specrosc. Rel. Phenom. 73 (1995) 25

[2] A. K. Livesey, G.C. Smith, J. of Elec. Spectroscopy 67 (1994) 439-961.

**AS-TuP3 Analysis Area Determination in Small Area XPS**, ***C.J. Blomfield***, *S.J. Hutton, S.C. Page, S.J. Coultas*, Kratos Analytical Ltd, UK

Currently, the accepted method of analysis area determination for small area XPS is to scan either the selected area spot or area illuminated by the X-ray beam over a well defined edge. The maximum signal is assumed to be 100% and the minimum signal 0%, the value used to determine the analysis area is then defined as the distance for the signal to change from 80% to 20% (or 84% to 16%) of these values.[1] This method has previously[2] been shown to produce total analysis areas approximately three times the diameter of that given by this "edge" measurement. An alternative approach of comparing the signal measured when an analysis is taken in the centre of an aperture of predetermined size has recently been shown to be another valid method for analysis area determination.[3] We have compared both of these methods for Kratos Axis Nova and Axis Ultra instruments which use a virtual probe approach, with the analysis area limited by both an area defining aperture and an angle defining iris to produce a Gaussian analysis area profile. The suitability of these methods and the implications to the true analysis area for the analyst will be discussed.

[1] ISO/TR 19319 Surface Chemical Analysis – Auger Electron Spectroscopy and X-ray Photoelectron Spectroscopy- Determination of lateral resolution, Analysis Area and Sample Area Viewed by the Analyser 2003

[2] Baer DR, Engelhard MH, Surf. Interface Anal 2000; 29 766

[3] Scheithauer U, Surf. Interface Anal 2008.

**AS-TuP5 Characterization of X-ray Photocathode in Transmission Mode at 3keV**, ***H. Ikeura-Sekiguchi***, National Institute of Advanced Industrial Science and Technology (AIST), Japan, *T. Sekiguchi*, Japan Atomic Energy Agency (JAEA), *M. Koike*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

X-ray photoelectron emission microscope (X-PEEM) combined with synchrotron radiation is one of the most promising techniques for real-time surface spectromicroscopy. When X-PEEM is used as an x-ray detector for a transmission x-ray microscope, information on the subsurface properties of thin samples is obtainable with high spatial resolution. For the purpose of application to X-PEEM imaging in transmission mode, X-ray induced electron emission properties from photocathodes were investigated. Experiments were performed at beamline BL-2 of the AIST synchrotron radiation facility TERAS in Tsukuba. The BL-2 is equipped with an Si(111) double-crystal monochromator. Back-surface secondary electrons were detected using a microchannel plate (MCP, Hamamatsu Photonics K.K.). Photocathode thin layers of Al with higher quality on a kapton film were produced using the helicon plasma sputtering system. Thickness dependence of total electron (mostly secondary electron) emission yields from back-surface of Al film is measured at 3 keV photon energy. Secondary electron escape depth of Al was estimated based on semiempirical equations and suitable photocathode thickness of Al was experimentally evaluated. Capability of the imaging technique using the transmission photocathode will also be discussed.

**AS-TuP6 Advanced Data Analysis for Surface Topography Characterization of Niobium Superconducting RF Accelerator Cavities**, *H. Tian*, College of William & Mary, *G. Ribeill*, North Carolina State University, *C.E. Reece*, Thomas Jefferson National Accelerator Facility, ***M.J. Kelley***, College of William & Mary

An unprecedented number and scale of particle accelerator projects are getting underway, most notably the 30-km plus long International Linear Collider. The dominant technology is based on superconducting niobium radio-frequency (SRF) cavities, powered to ever-increasing acceleration gradients. The rf energy's shallow penetration depth – few tens of nm – lends great importance to cavity interior surfaces. Interior surface etching to remove mechanical damage leaves surface topography, including protrusions of varying sharpness. These may promote RF magnetic field entry, locally quenching superconductivity, so as to degrade cavity performance. A more incisive analysis of surface topography than the widely-used average roughness is needed. We introduce a Power Spectral Density (PSD) approach based on Fourier analysis of surface topography data acquired by both stylus profilometry and atomic force microscopy (AFM). We report the evolution of the Nb surface PSD as a function of applied etching and polishing steps, resulting in a novel quantitative description of roughness. An important aspect of the impact of processing on SRF performance is made significantly clearer.

### AS-TuP7 XPS Analysis of a Complex Metal Oxide Coatings on Stainless Steel: Depth Profiling,

***H.M. Meyer, III***, Oak Ridge National Laboratory

A low-temperature process was used for depositing complex metal oxide films onto stainless steel (SS304). Some films contained Fe, Cr, Si, and Ca, others contained Sm and Ce, and still others had Fe and Zr. The coating process consisted of dipping the SS coupons once or several times into a patented liquid followed by a thermal treatment at temperatures comparatively lower than those experienced during more conventional CVD or PVD coating processes. This liquid plus thermal treatment coating process produced surface films ranging from 50 to 500 nanometers (nm), depending on the number of dipping steps. Coated parts have been tested in a variety of environments ranging from corrosive to abrasive and have shown enhanced surface properties leading to better performance. Thermo Fisher Scientific's K-Alpha XPS instrument was used for characterizing the through-depth composition of these films. This instrument has a micro-focused mono-chromatic Al ka x-ray source (spot size 30-400 microns), Ar ion sputter gun, and a charge compensation system utilizing both low energy electrons and low energy Ar ions. Depth profiles were obtained on these relatively thick films (500 nm) at high acquisition rates by acquiring the data at low energy resolution (i.e. high pass energy). Post-profiling data processing allowed the low resolution data to be transformed to high energy resolution using the Avantage Data Processing software (v.3.85) and special energy de-convolution routines. This method allowed rapid data acquisition along with detailed determination of through-depth chemistry via high energy resolution core level data. The post-processed data will be compared to Auger depth profiles and XPS data obtained using high energy resolution data acquisition at much slower acquisition rates. Research sponsored by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of FreedomCAR and Vehicle Technologies, as part of the High Temperature Materials Laboratory User Program, Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U.S. Department of Energy under contract number DE-AC05-00OR22725.

### AS-TuP8 Structural Characterization of Ag Nanoparticles Embedded in $TiO_2$ Thin Films Prepared by Means of RF-Magnetron Sputtering,

***V. Moellmann***, University of Paderborn, Germany, *P. Keil, J. Zuo, H. Itani, T. Titz,* Max-Planck-Institut fuer Eisenforschung GmbH, Germany, *G. Grundmeier*, University of Paderborn, Germany

The combination of nanometer-sized metal particles and semiconductor matrix materials displays size and matrix dependend properties. These nanocomposite materials have been attracting much attention in recent years because of their unique catalytic behaviour, nonlinear optical properties or selective optical absorption and reflection. Usually, the synthesis route strongly influences the properties of the embedded nanoparticles, especially in terms of the size, structure, crystal morphology, degree of crystallinity and the nature of the sample surface, which are important for the functional properties of thin nanocomposite films. Silver nanoparticles embedded in TiO2-films have a high potential for applications in the fields of solar energy conversion, photocatalysis, chemical and biological sensing or antibacterial coatings. RF-sputtering method is one of the most feasible methods due to its inherent versatility and the capability of obtaining a homogeneous surface coverage at low temperatures under controlled processing conditions. In the present study, TiO2 films with embedded Ag nanoparticles were prepared by means of RF-magnetron sputter deposition and subsequent annealing. We applied grazing incidence X-ray absorption spectroscopy amongst other analytical methods including AFM or SKPFM to investigate the effects of deposition on the size and structure, crystal morphology and the degree of crystallinity of the embedded Ag nanoparticles as well as the TiO2 matrix material. The influence of the deposition parameters on the structure of the nanocomposite films and on its optical properties and applications like reversible photochromic transformations or antibacterial coatings are presented.

### AS-TuP10 Quantitative Analysis of Si-Ge Alloy Films and Compositional Depth Profiling of Si/Ge Multi Layers Using SIMS,

*K.J. Kim, **J.S. Jang**,* Korea Research Institute of Standards and Science*, T.E. Hong,* Korea Basic Science Institute*, H.J. Kang*, Chungbuk National University, Korea

Although secondary ion mass spectrometry (SIMS) is a powerful technique for the in-depth analysis of solid materials, it is difficult to apply for the quantitative analysis of major components due to severe matrix effect. In addition, the different ionization probability caused a significance interface artefact in the interfaces between two metals due to different ionization yields.[1] However, if the variation of ionization probability is linear in a specific composition range, the interface artefact can be compensated.[2] A Si/Ge multilayer, Si-Ge alloy multilayer films and Si-Ge alloy films were grown on Si (100) wafers by ion beam sputter deposition. The compositions of Si-Ge alloy films were analyzed by SIMS and compared with the nominal compositions obtained by Rutherford backscattering spectroscopy. The quantification results were found to be highly improved by oxygen ions with higher energy. In SIMS depth profiles of Si/Ge multilayers using oxygen ion beam, the interfaces are difficult to be defined because of the interface artifacts in the Si/Ge and Ge/Si interfaces due to the matrix effect. However, the interfaces could be clearly defined after conversion of the profiles to composition profiles using relative sensitivity factor determined from a SIMS depth profile of a Si52.4Ge47.6 alloy film. The etching rate of a Si layer is much slower than that of Ge layer because of the formation of SiO2 layer during O2+ ion sputtering.

[1] K. J. Kim and D. W. Moon, Appl. Phy. Lett., 60, 1178-1180 (1992).

[2] K. J. Kim, D. Simons, and G. Gillen, Appl. Surf. Sci. 253, 6000-6005 (2007).

### AS-TuP11 Quantitative Multi-Technique Analysis of Silicon Germanium Semiconductors,

***R.E. Davis****, M. Hatzistergos, B.M. St. Lawrence, T.L. Tai, A.G. Domenicucci, A Madan, T.L. Pinto, P. Ronsheim, Z. Zhu, A.R. Turansky, J.R. Holt, M. Hopstaken, T.N. Adam*, IBM Corp.

In its continuing quest for higher density and performance, the semiconductor industry, in addition to shrinking circuit dimensions, has also turned to novel engineered materials. This paper will describe one such material, epitaxially grown SiGe, and the significant challenges it has brought both to process engineering as well as micro-analysis. It was noted that the mobility of carriers can be enhanced by the selective local application of stress, either compressive or tensile. One way compressive stress can be achieved for pFETs is by incorporating a controlled amount of Ge into the Si lattice, and has been the focus of much recent activity.[1-3] Precise control of this enhanced mobility requires quantitative monitoring of the SiGe, for composition, structure and stress. In addition to the normal process concerns about consistency, uniformity, and throughput, the SiGe deposition process exhibits behavior referred to as "loading effects". In essence, the composition, structure and deposition rate depend on the overall area of exposed Si, as well as its feature size and immediate vicinity. These requirements for analysis have necessitated the careful application of a variety of micro- and bulk characterization techniques, including AES, SIMS, AFM, RBS, EPMA, Ellipsometry, SEM, TEM, XRD, XRR, and Raman techniques. Results will be presented using the AES, XRD and SIMS techniques for this demanding application.

[1] "Design of High Performance PFETs with Strained Si Channel and Laser Anneal", Z. Luo, Y. Chong1, J. Kim3, N. Rovedo, B. Greene, S. Panda, T. Sato4, J. Holt, D. Chidambarrao, J. Li, R. Davis, A. Madan, A. Turansky, O. Gluschenkov, R. Lindsay2, A. Ajmera, J. Lee1, S. Mishra1, R. Amos, D. Schepis, H. Ng, and K. Rim, IEDM Tech Digest, 495 (2005).

[2] "Impact of In-situ C Doping on Implant Damage and Strain Relaxation in Epitaxial SiGe layers on Si", Jinping Liu,* Anthony Domenicucci,** Anita Madan,** Jinghong Li,** Judson Holt,**, Richard Murphy, Andrew Turansky, Robert E. Davis, Lindsay E. Burns, and John Sudijono*, MRS 2006 Spring Meeting

[3] "Systematic Characterization of Pseudomorphic (110) Intrinsic SiGe Epitaxial Films for Hybrid Orientation Technology with Embedded SiGe Source/Drain", Qiqing (Christine) Ouyang*, Anita Madan, Nancy Klymko, Jinghong Li, Richard Murphy, Horatio Wildman, Robert Davis, Conal Murray*, Judson Holt, Siddhartha Panda, Meikei Ieong and Chun-Yung Sung, MRS Proceedings 913, pp. 13-18 (2006).

### AS-TuP12 Atmospheric Plasma Surface Modification Analysis by Energy Resolved Molecular Beam Mass Spectrometry and SIMS,

***P.J. Hatton****, Y. Aranda Gonzalvo, G.A. Cooke, T.D. Whitmore, D.L. Seymour, C.L. Greenwood, J.A. Rees*, Hiden Analytical, UK

Electrical plasmas can be readily produced at atmospheric pressure and have relatively low running costs. They are ideal for a variety of industrial process applications for many materials. Processing using non-thermal atmospheric plasma currently extends to areas such as surface cleaning and functionalisation, plasma activation, tissue engineering and sterilisation. To aid in understanding the mechanisms involved in plasma/surface interaction we present results of both plasma measurements and surface composition studies for a range of materials treated using an atmospheric dielectric surface barrier discharge (DSBD). The plasma properties were determined using an energy-resolved molecular beam mass spectrometer (ERMBMS). The surface compositions of the materials before and after treatment were compared using a static SIMS instrument. The dielectric surface barrier discharges were operated using helium gas and applied to molybdenum, silicon wafers and printed circuits. Silicon test pieces were treated using hydrofluoric acid to produce a strongly hydrophobic, hydrogen-terminated surface. The hydrophobicity of the surfaces could be significantly reduced by short exposure to certain plasma conditions. Static SIMS analyses of these surfaces showed a significant reduction in the observed SiH+ signal and an accompanying increase in the Si and the reactive silanol groups [Si-OH]. ERMBMS consists of an energy mass spectrometer (QMS) with a differentially pumped three-stage inlet system [1]. Mass spectra of the ions generated in the DBSD source show a high concentration of monoatomic and diatomic oxygen. Analysis of the ion energy reveals that the ions are fully thermalized, with energies close to 0.03 eV. ERMBMS analyses of the plasmas provided information on the relative contributions of ionic and radical species to the changes in the surface structure and the combination of data from the two diagnostic techniques contributes to our general understanding of such plasma/surface processing.

Reference [1] Y.Aranda Gonzalvo, T.D. Whitmore, J.A. Rees, D.L.Seymour, E. Stoffels, 2006 J.Vac.Sci. Technol., A 24 550. Keywords: energy mass spectrometer, dielectric surface barrier discharge, atmospheric plasmas, SIMS.

**AS-TuP13 A Mutual Calibration Method to Certify the Thickness of Nanometer Oxide Films***, **K.J. Kim**, Y.S. Kim, J.S. Jang, J.W. Kim*, Korea Research Institute of Standards and Science

The reliable measurement of ultra-thin gate oxide thickness below 1 nm is one of the most important analysis issues for the next generation semiconductor devices as shown in the recent international technology roadmap (ITRS). X-ray photoelectron spectroscopy (XPS) is an ideal candidate for the thickness measurement of ultra-thin films because of the surface sensitivity due to the shallow detection depth of low energy photoelectrons. However, XPS needs a standard film to determine the electron attenuation length because XPS is not an absolute method to determine the original thickness of overlayer films. In a recent study on the measurement of SiO2 film thickness on a silicon substrate, the thicknesses measured by various methods showed large offset values, giving an apparent thickness when the real thickness is extrapolated to zero. Compensation of these offset values is a key solution for the establishment of the traceability in the measurement of SiO2 film thickness. In this study, a mutual calibration method is suggested as a new method to certify the thickness of SiO2 films on Si by compensating for the offset values. In a linear plot of the thicknesses measured by x-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) of a series of SiO2 films with different thicknesses, the offset value of TEM and the thickness scale of XPS can be mutually calibrated. Using this method, the XPS photoelectron attenuation length can be well defined and XPS becomes traceable in the measurement of the thickness of SiO2 films.

**AS-TuP14 Imaging Surface Organics via Single Photon Secondary Neutral Mass Spectrometry with Tunable Synchrotron VUV***, **L.K. Takahashi**, J. Zhou, M. Ahmed,* Lawrence Berkeley National Laboratory*, S.R. Leone,* University of California, Berkeley*, K.R. Wilson*, Lawrence Berkeley National Laboratory

Elemental chemical imaging of surfaces on the sub-micron scale with Secondary Ion Mass Spectrometry (SIMS) has yielded much new and tantalizing information. However, the method is limited in its application to more fragile organic molecules due to extensive fragmentation, which results in complicated mass spectra that are difficult to analyze. Furthermore, the sensitivities of different chemical species in SIMS are highly dependent on the local chemical environment, meaning that relative intensities in the mass spectra do not reflect the actual chemical abundances at the surface. In Secondary Neutral Mass Spectrometry (SNMS), ejected neutrals are post-ionized, effectively decoupling the desorption and ionization steps. The resulting mass spectra are less dependent on the local chemical environment. Fragmentation of organic molecules, however, has remained a problem. The ionization potentials of most organic molecules are around 9-11 eV, and commercial tabletop lasers usually have lower photon energies than this, necessitating multiphoton ionization. This ionization method imparts excessive energy to the neutral molecules which can fragment organic chemical species. Here we present a new method utilizing continuously tunable VUV synchrotron light for single photon post-ionization of secondary organic neutrals. By ionizing just above the threshold, it has been shown that fragment free mass spectra of organic molecules can be obtained. The tunability of the light also allows for isomer identification by their characteristic ionization energies and associated fragments. While the experiment is still in its early stages, preliminary results have yielded unique photoionization efficiency curves for different organic molecules. With further improvements, single photon VUV-SNMS can become a powerful tool capable of providing localized chemical information on real-world heterogeneous organic systems such as microbial cells and aerosols.

**AS-TuP17 Temperature Effect on Chemical and Physical Stability of Low Pressure Plasma Polymerised Coatings for Biological Applications***, **S.I. Cho**,* Pusan National University, South Korea*, M. Dhayal*, University of Washington

The effects of substrates heating on chemical and physical stability of plasma polymerised acrylic acid films were studied. The change in surface chemistry and surface morphology were characterised by X-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). XPS result showed that C(=O)OX functionality was unstable with the substrate heating temperature whereas C-OX and C=O functionalities were quite stable for 400oC. Small changes in the surface roughness were observed when substrate was heated upto 100oC. Higher temperature heating had created well structured patterns at the surface. Effect of these patterns and change in surface functionalities on cell growth and no-specific adsorption of proteins will be discussed.

**AS-TuP18 The Electronic Structure of Pristine Copper-Hexadecafluorophthalocyanine (F16CuPc) from Resonant X-ray Emission Spectroscopy***, A. DeMasi, L.F.J. Piper,* Boston University*, **Y. Zhang**,* University of Nevada, Las Vegas*, K.E. Smith*, Boston University

Metal-based phthalocyanines (M-Pc) have become both fundamentally and technologically important.[S. Heutz et al., Adv. Mat. 19, 3618 (2007)] Here we report of recent synchrotron-based soft x-ray spectroscopy measurements of copper hexadecafluoro phthalocyanine (F16CuPc). Resonant x-ray emission spectroscopy (RXES) enables bulk, element and orbital-specific information of states near the Fermi level. We have examined the C, N, and F K-edges of thin films deposited in-vacuo, measured within our experimental endstation at the undulator beamline X1B at the National Synchrotron Light Source. Direct comparisons are made to earlier x-ray absorption and emission spectroscopy measurements of CuPc.[J. Downes et al., Chem. Phys. Lett. 390, 203 (2004)]. We focus on the C K-edge RXES of F16CuPc, and make comparisons with recent ultraviolet photoemission spectra and spin-polarized theoretical computations of non-fluorinated CuPc and F16CuPc.

**AS-TuP19 XPS Analysis of Organic Materials Etched by Charged Water Droplet Impact***, **Y. Sakai**,* University of Yamanashi, Japan*, Y. Iijima,* JEOL Ltd.*, R. Takaishi, D. Asakawa, K. Hiraoka*, University of Yamanashi, Japan

A giant cluster ion impact method, electrospray droplet impact (EDI) ionization, has been developed for matrix-free secondary ion mass spectrometry.[1] EDI utilizes the electrospray charged water droplet as the extremely high-momentum projectiles. The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure are passed through an orifice into the vacuum chamber, transported into a quadrupole ion guide, accelerated by 10kV after exiting the ion guide and impact on a target. Roughly, the charged water droplets may be represented as $[(H_2O)_{90000}+100H]^{100+}$ with mass of~$1.6x10^6$ u. The kinetic energy of impacting projectile is ~$10^6$ eV.[2] The polymer samples (PET, PMMA, PS) etched by EDI were evaluated by X-Ray Photoelectron Spectrometer (XPS: JEOL JPS-9200). A comparative study for PET, PMMA and PS etched by $Ar^+$ ion and EDI was made. For the surfaces of PET, PMMA and PS etched by $Ar^+$ ion, the deoxygenation and graphitization were found. The degradations of the polymers by the ion sputtering are slightly suppressed by using the low energy ion or the cluster ion. But, the effect of suppressing degradations was depended on the polymers. On the other hand, the deoxygenation, and graphitization were not observed on the surfaces of PET, PMMA and PS etched by EDI. It supposed that the kinetic energy of impinging water droplet at the moment of impact on the target by EDI is efficiently converted to the internal energies of water molecules in the selvedge of the colliding interface. The rest is dissipated as shock waves propagating through the target and the water droplet. This verifies that EDI is capable of no degradations of the polymer surface etching. The other experimental results of EDI applied to metals, semiconductors will be given. Acknowledgement: This work was supported by the Japan Science and Technology Agency.

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[2] K.Hiraoka, K.Mori, D.Asakawa, J.Mass Spectrom., 41 (2006) 894.

**AS-TuP20 XPS Study of Nitrogen Chemical Structure in DNA and Related Molecules***, **I. Ishizaki**, N. Sanada, S. Iida, M. Suzuki, Y. Ohashi,* ULVAC-PHI, Inc., Japan*, G. Hayashi, K. Nakatani*, Osaka University, Japan

Although recent XPS instrumental developments would provide high S/N ratio and much improved resolution for better interpretation of chemical structures,[1] relatively little application has been reported for bio materials including DNA. It has been reported that XPS N 1s lines of DNA nucleobases were affected by their chemisorption on Cu, and the peak shift was assigned as the dehydrogenation.[2] May et al.[3] reported in detail on XPS lines for several kinds of DNA and related materials, however, assignment of the N 1s lines in DNA was not fully elucidated as far as our knowledge. In this study, therefore, we studied nitrogen chemical structure of DNA-related molecules using XPS, cluster TOF-SIMS, and DFT calculations. The DNA-related molecules reported here include adenine (A), guanine (G), thymine (T), cytosine (C), and hypoxanthine (I), and their nucleotides, poly(nucleotides), single and double strained DNA molecules, and a DNA microarray. XPS N 1s lines had little differences between nucleobase and nucleotide for each series. On the other hand, they were sharply different between nucleotides and poly(nucleotides) for A, G, and C, but no obvious differences are found for T and I. Comparative study with G and I bases indicated that primary amine ($-NH_2$) group in the molecule played an important role on the chemical state changes of nitrogen. DFT calculation results of model nucleobase crystals and single-strained DNAs will also be discussed.

[1] for example, M. C. Biesinger, et al. Surf. Interface Anal., 36 (2004) 1550.

[2] M. Furukawa et al. Surf. Sci., 601 (2007) 5433.

[3] C.J. May, et al. Anal. Chem., 76 (2004) 1114.

**AS-TuP22 Root-Cause Failure Analysis of Anneal-Chamber Reflector Plates using Advanced XPS and TEM/EDX Applications***,* ***C. Lazik****, M. Jin, Y. Uritsky, L. Terry*, Applied Materials, Inc.

Delamination failures were observed on reflector plates in Vantage RTP systems during start-up in late-2006. Root-cause analysis was required to complete the current tool sign-off and to identify suspect parts/spares in the field. The reflector plate supplier revealed they had upgraded their e-beam evaporation chamber in June, 2006, but that the coating characteristics, reflectivity and adhesion strength, had not changed. The product support team provided reflector plates manufactured before and after the e-beam evaporation chamber upgrade to the Defect and Thin-Film Characterization Laboratory (DTCL) to identify any differences in the coatings that may explain the failure. Using X-ray Photoelectron Spectroscopy (XPS) and Transmission Electron Spectroscopy (TEM), DTCL identified titanium poisoning within a ~30A oxide layer at the base of the adhesion film on all of the failed parts. Results enabled the product support team to pinpoint the failure mechanism, locate the contamination source in the supplier's hardware, and implement new quality control inspection tests/procedures for new, incoming reflector plates.

**AS-TuP23 Microstructural Transformations of Ultrathin TiDy/Pd Bi-Layer Films Evaporated on Si(100) and Quartz Induced by Vacuum Annealing***,* ***E.G. Keim****,* University of Twente, The Netherlands*, W. Lisowski,* Polish Academy of Sciences*, M.A. Smithers*, University of Twente, The Netherlands

Thin $TiD_y$/Pd bilayer films[1] can be applied as a useful source of deuterium used in chemical and energetic reactions. Evolution of hydrogen from such material is realized by high-temperature annealing. Main question is to what degree structural changes occur within both the substrate and the ultrathin $TiD_y$/Pd bi-layer film as result of annealing induced decomposition of the titanium deuteride phase. In this paper we present the results of a combined SEM/TEM study dealing with these questions. The results are compared for two ultrathin $TiD_y$/Pd films evaporated on quartz and Si(100), respectively. Ultrathin $TiD_y$/Pd films (10 - 20 nm thick TiDy films covered by 10 - 20 nm thick Pd films) were prepared in a UHV glass system.[2] Decomposition of the titanium deuteride phase in the TiDy/Pd film during annealing, was monitored in situ by TDMS,[3] all other analysis ex situ. It was found that annealing of the $TiD_y$/Pd films, evaporated on various substrates, leads to significant transformations within the films studied. SEM images disclosed various stages of rearrangement of the surface morphology in both films. Energy Filtered TEM analyses of cross-section images as well as EDX point analyses revealed extensive inter-diffusion of Ti and Pd within both Ti-Pd bi-layer films. Moreover, the EF-TEM Si elemental map displayed also a significant penetration of Si atoms from the Si substrate into the Ti area of the Ti-Pd film.

[1] W. Lisowski, E.G. Keim, A.H.J. van den Berg, M.A. Smithers, Anal. Bioanal. Chem. 385 (2006) 700.

[2] W. Lisowski, Vacuum, 54, 13 (1999).

[3] W. Lisowski, E.G. Keim and M.A. Smithers, J. Vac. Sci. Technol. A21, 545 (2003).

**AS-TuP24 Analysis of the Line Shape on Layer-Resolved Photoemission Signals in Determining the Absolute Coverage of Atomically Flat Metallic Thin Films***,* ***D.-A. Luh****,* National Central University, Taiwan*, C.-M. Cheng, K.-D. Tsuei*, National Synchrotron Radiation Research Center, Taiwan

An important application of nanotechnology is the construction of nanodevices for specific problems. Size is typically the parameter that engineers vary while adjusting the physical properties of nanodevices. Because of electronic confinement from the boundary, the properties of a nanostructure depend strongly on its size; this effect is called the quantum size effect (QSE), which has been reported on various physical properties. To study the QSE properly, one must determine and control the size of nanostructures with an atomic resolution. Failure to do so not only makes the analysis of the QSE less confident, but also makes the process of manufacturing nanostructures unreliable. To address this issue, we report a technique to determine film coverage precisely by analyzing layer-resolved signals in one photoemission spectrum. We demonstrate that the coverage of a metallic thin film on the (111) surface of noble metals is determined precisely on analyzing its layer-resolved confined states measured with angle-resolved photoelectron spectra. In our work, the surface state on a Ag film of 1~4 ML and the quantum well states on a Ag film of 7~13 ML on Au(111) were analyzed with atomic resolution. Through analysis of the line shape with tabulated binding energies, we determined precisely the absolute Ag coverage of a Ag/Au(111) film on analyzing a single spectrum. For this technique to work, photoemission cross sections for signals corresponding to adjacent thicknesses are assumed to be similar, and the intensities of the signals are directly proportional to the domain area of their corresponding film thicknesses. This assumption disagrees with previous authors who reported the variation of photoemission cross sections with photon energy in many systems. To investigate the prospective inconsistency, we performed energy-dependent photoemission measurements on atomically flat thin films with well-controlled coverage. Our results show that the line-shape analysis is valid with an absolute error in the measured absolute coverage within 0.1 ML for a Ag film on Au(111) when the photon energy is appropriately chosen. The experimental procedure employed in our work not only validates the line-shape analysis but also serves as a routine to determine an appropriate photon energy for the line-shape analysis. The line-shape analysis with absolute error possesses great advantages over other techniques with relative error, especially for a higher film coverage.

**AS-TuP25 3-Dimensional XPS Imaging of Surface Nano-structures; A New Technique***,* ***S. Tougaard****, S. Hajati*, University of Southern Denmark

XPS energy spectra vary characteristically with the depth distribution of electron emitting atoms on the nano-scale. This is the basis for the by now well known and widely used method[1] to non-destructively determine atomic depth distributions with nano-meter resolution by analysis of the inelastically scattered electrons associated with the XPS peak. A new algorithm which is suitable for automation was suggested recently.[2] For each XPS signal, this algorithm determines the total amount of the corresponding atoms within the outermost ~ 10 nm and it also determines their depth distribution. The validity of the algorithm was demonstrated experimentally by comparison to more elaborate quantification methods.[3] In addition, software that can automatically analyze several thousand spectra corresponding to the situation in XPS imaging is developed. The software produces nondestructively a 3-D image of the surface with nanometer depth resolution. The practical applicability for XPS imaging was recently demonstrated.[4-5] As an example we have demonstrated a quantitative test[4] of the algorithms ability to produce images of Ag taken from a series of samples with increasing thicknesses of plasma patterned Octadiene (2, 4, 6 and 8nm) on Ag substrates. The obtained images of the amount of silver atoms in the outermost few nano-meters of the samples were in good agreement with the nominal thicknesses. For a given sample, different sectioning of depth distributions of atoms were made which clearly prove the ability of the method for quantitative and nondestructive 3-D characterization of nano-structures. In ref [5], 3D images of thermally patterned oxidized silicon made through a photolithographic mask were produced and it was shown that 3-D images of the Si, O, and C atoms were complementary. In the talk we will summarize the technique and discuss its limitations and capabilities.

[1] S. Tougaard Surf. Interf. Anal. 26, 249 (1998)

[2] S. Tougaard, J. Vac. Sci. Technol. A21, 1081 (2003)

[3] S. Tougaard, J. Vac. Sci. Technol. A23, 741 (2005)

[4] S. Hajati, S. Coultas, C Blomfield and S. Tougaard, Surf. Interf. Anal. 40, 688 (2008)

[5] S. Hajati, J. Walton, N. Fairley, and S. Tougaard, Surf. Sci. (2008). In press.

## Biomaterial Interfaces
## Room: Hall D - Session BI-TuP

### Biomaterials Interfaces Poster Session with Focus on Cells and Proteins at Interfaces

**BI-TuP1 Human Serum Albumin Adsorption to Expanded Polytetrafluoroethylene***,* ***E.S. Leibner****, N. Barnthip, W. Chen, C.R. Baumrucker, J.V. Badding,* The Pennsylvania State University*, M.V. Pishko,* Texas A&M University*, E.A. Vogler*, The Pennsylvania State University

Analytical protocol greatly influences measurement of human-serum albumin (HSA) adsorption to commercial expanded polytetrafluororethylene (ePTFE) exhibiting superhydrophobic wetting properties (water contact angles in excess of 150°). Degassing of buffer solutions and evacuation of ePTFE adsorbent to remove trapped air immediately prior to contact with protein solutions are shown to be essential steps that assure reproducible measurement of HSA adsorption. Results obtained with ePTFE as a superhydrophobic test material suggest that vacuum degassing should be generally applied in the measurement of protein adsorption to any surface exhibiting superhydrophobicity. Solution depletion quantified using radiometry (I-125 labeled HSA) or electrophoresis (unlabeled HSA) yield different measures of HSA adsorption, with nearly seven-fold higher surface concentrations of unlabeled HSA measured by the electrophoresis method. This outcome is attributed to the influence of the radiolabel on HSA hydrophilicity which decreases radiolabeled-HSA affinity for a hydrophobic adsorbent in comparison to unlabeled HSA. These results indicate that radiometry underestimates the actual amount of protein adsorbed to a particular material. Removal of radiolabeled HSA adsorbed to ePTFE by 3X serial buffer rinses also shows that the remaining "bound fraction" was about seven-fold lower than the amount measured by radiometric depletion. This observation implies that measurement of protein bound after surface rinsing significantly underestimates the actual amount of protein concentrated by adsorption into the surface region of a protein-contacting material.

**BI-TuP2 The Role of Surface Chemistry in poly-L-lysine Mediated Alginate Adsorption**, ***K.T. Queeney***, *J.E. Brown*, *E.K. Davis*, *C. Franqui*, Smith College

Adsorption of polysaccharides to solid substrates, an essential component of biofilm formation, is generally protein-mediated. Lysine-rich proteins, in particular, are known to have significant adhesive properties in these systems. This work uses poly-L-lysine (PLL) as a model protein to explore the role of the underlying substrate in protein-mediated adsorption of alginate, a negatively-charged polysaccharide. We have prepared films of varying PLL coverage on two types of surfaces: hydrophilic, negatively-charged silica and a hydrophobic, electrically neutral alkylsilane monolayer. PLL coverage on the hydrophilic surface is controlled by varying the ionic strength of the adsorption solution, while PLL coverage on the hydrophobic surface is controlled by varying the molecular weight of the PLL. By a combination of techniques--primarily ellipsometry, dynamic contact angle goniometry and atomic force microscopy--we demonstrate that not only the film morphology of the PLL but also its effect on subsequent alginate adsorption is highly sensitive to the surface chemistry of the underlying substrate. For example, PLL films on silica are more discontinuous at low and high ionic strength, and alginate adsorption is highly influenced by this discontinuity, which allows for repulsive electrostatic interactions between the surface and the alginate. In contrast, while there is an increase in PLL film discontinuity as a function of increasing PLL molecular weight, alginate adsorption appears largely insensitive to these changes in PLL film morphology. Through quantitative analysis of the advancing contact angles on both these (chemically heterogeneous) surfaces we demonstrate unequivocally that the PLL/solution interface is highly dependent on both substrate surface chemistry and PLL adsorption conditions.

**BI-TuP3 Time of Flight Secondary Ion Mass Spectrometry Characterization of the Surface Polysaccharides of Group B Streptococcus**, *T. Nguyen*, Oregon State University, ***J.R. Hull***, *D.G. Castner*, University of Washington NESAC/BIO

Group B Streptococcus (GBS) is a leading cause of sepsis and meningitis in neonates and immunocompromised adults in western countries. The surface of GBS is well characterized by standard microbiological techniques and therefore makes a good test system for analyzing bacteria using Time of Flight Secondary Ion Mass Spectrometry. GBS is layered with a capsule composed of five distinct polysaccharides containing glucose, galactose, N-acetylneuraminic acid, rhamnose, and N-acetylglucosamine. The capsule makes up 10 to 30% of the dry weight of the microorganism and is only present on the surface. In this work, the five monosaccharides, pure capsule from type III GBS, and UV killed GBS strain COH1 and acapsular GBS strain COH1-13 were investigated. It was observed that the pure monosaccharide fragmentation patterns followed $C_xH_{2x}O_x^+$, and that the largest fragment observed of the monosaccharides was with the loss of $H_2O$, $OH^-$ or $H_3O^+$. The presence of sodium, magnesium, and calcium in the purified samples made direct comparison with the pure monosaccharides difficult due to cationization effects. Spectra from clusters of GBS and single organisms were acquired using the high mass resolution imaging mode and constructing a spectrum from a region of interest. The biggest differences between COH1 and COH13 were seen in the high mass region of the spectra.

**BI-TuP4 Hydrogels with KGF**, ***J.A. Appawu***, *J.A. Gardella*, University at Buffalo: The State University of New York

XPS and TOF-SIMS are techniques that can be used to quantify the uptake and release of proteins from polymers. Hydrogels are cross-linked hydrophilic polymers used in localized delivery of growth factors through pores defined by type and density of cross-links. Therefore uptake and release are diffusion controlled. Keratinocyte growth factor 1(KGF-1) is known to promote re-epithelialization after skin injury and stimulate the proliferation of skin cells. Inadequate amounts of growth factors can result in inefficient healing. In this study, (hydroxyethyl methacrylate ) (HEMA) hydrogels 3% and 6% were prepared with varying cross-link densities to answer three key questions:1) What is the optimal concentration of KGF-1 for cell adhesion, 2) Are HEMA hydrogels with specific structural properties viable for cell proliferation, and 3) What is the amount and time course of released KGF-1 present on the surface? Hydrogels were cut into equal areas to determine the amount of KGF-1 protein taken into and released from the hydrogels by fluorescence spectroscopy. XPS was used to confirm the quantity of KGF-1 on the surface and bulk by varying the take-off angle (TOA). The nitrogen atomic concentration was used to track the protein since nitrogen is present only in KGF-1. The amount of KGF-1 was higher in the 3% hydrogel due to a swelling ratio of 58.5% compared to 40.5% for the 6% hydrogel. Cell adhesion experiments have shown that 80-90% of HaCaT cells successfully adhere to the surface of the KGF-1 imbibed hydrogels and fluorescence microscopy proved that the cells were alive. TOF-SIMS has been used in depth profiling to confirm the XPS results.

Mahoney C. M., Yu J., Fahey A., and Gardella J. A. Jr. SIMS Depth Profiling of polymer blends with protein based drugs. Applied Surface Science (2006) 6690-6614. Pierce G.F. et. al. Stimulation of All Epithelial Elements during Skin Regeneration by Keratinocyte Growth Factor. J. Exp. Med. (1994) 179, 831-840. Tsuboi R. et al. Keratinocyte Growth Factor (FGF-7) Stimulates Migration and Plasminogen Activator Activity of Normal Human Keratinocytes. J. Invest. Dermatol. (1993) 101, 49-53. Greenhalgh D. G. The role of growth factors in wound healing. J. Trauma. (1996) 41, 159. Mahoney C. M., Yu J., and Gardella J. A. Jr. Depth Profiling of Poly(L-lactic Acid)/TriBlock Copolymer Blends with Time-of-Flight Secondary Ion Mass Spectrometry. Anal. Chem. 2005 77, 3570-3578.

**BI-TuP6 Novel Patterned Protein Assay To Measure Differential Extracellular Matrix Protein Affinities for Cellular Attachment and Axonal Outgrowth**, ***W.M. Theilacker***, *A.L. Styer*, *H.P. Bui*, University of Delaware, *D.E. Willis*, *J.L. Twiss*, Alfred I. DuPont Hospital for Children, *T.P. Beebe, Jr.*, University of Delaware

Cellular preference for extracellular matrix (ECM) proteins was assayed on patterned surfaces presenting two ECM proteins that compete for cell attachment and proliferation. Microcontact printing techniques were used to modify silicon substrates with alternating 40-um-wide stripes of the ECM proteins fibronectin and laminin. The spatial distribution of both proteins on the patterned surfaces was measured by epi-fluorescence and Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS). Attachment and outgrowth of dorsal root ganglia (DRG) neurons and neuron-like pheochromocytoma (PC12) cells on striped substrates were analyzed up to 4 days. At each time point, three patterned samples were fixed and immunostained prior to fluorescence imaging. Images were analyzed for the number of cells attached to each protein region and the number and length of neurite extensions. Results indicate for PC12 cells, an approximately equal number of cells on fibronectin and laminin stripes after 24 hours in cell culture. However, from 48 hours to 96 hours, the number of cells on laminin versus fibronectin continually increased. By 96 hours, 80 percent of the PC12 cells were attached to laminin versus fibronectin. Preliminary results for DRG neurons suggest a similar trend, in addition to the influence of Schwann cells, which are known to influence DRG neurite outgrowth.

**BI-TuP7 XPS Analysis of Protein Adsorption on Bioprocessing Materials**, ***R.A. Zangmeister***, National Institute of Standards and Technology

Protein therapeutics, a fast-growing category of biotech drugs, is adversely affected by protein aggregation. Aggregation can decrease the safety and efficacy of the therapeutic biologic protein product. Currently, the cause of protein aggregation is not clearly understood. The adsorption of protein therapeutics to bioprocessing materials used in production, storage and delivery may create nucleation sites for further protein aggregation. X-ray photoelectron spectroscopy was used to analyze protein adsorption on bioprocessing materials to screen for those with increased probability of contributing to aggregation of the protein therapeutic. The standard overlayer model and protein labeling were used to estimate the thickness of adsorbed protein layers.

**BI-TuP8 Highly Sensitive Probe of Crystalline Sub-Micron Sized Domain Structures in Amorphous Material**, ***H.B. de Aguiar***, *S. Roke*, Max-Planck-Instiut fuer Metallforschung, Germany

Mixtures of solid compounds or phases occur in a wide variety of chemical processes. Nucleation, crystallization and separation of phases are generally integrative steps in the production of polymer compounds, pharmaceuticals and in many other chemical processes. Many techniques used for analyzing mixtures of medium and ingredients in-situ rely on the interaction of photons with the mixture.[1] Such a situation occurs in solid/solid dispersions, where two different phases coexist, as in the case of most polymers which are known to consist of crystalline domains embedded in an amorphous phase. For instance, Wide-Angle X-Ray Diffraction (WAXS) and Small-Angle X-Ray Scattering (SAXS) are used together to obtain crystallite structure, size and fraction, being limited only by the level of background signal relative to the signal itself. We developed a new technique to study crystalline domains dispersed in an amorphous phase through nonlinear optical Vibrational Sum-Frequency Generation (VSFG) Scattering.[2] VSFG is a second-order nonlinear optical process, which is forbidden in centrosymmetric media (e.g. liquids, amorphous solids). We show the higher sensitivity of VSFG scattering to microspheres (MS) consisted of crystalline and amorphous phase. We studied the scattering pattern of some chiral polymers, namely Poly(Lactic Acid) (PLA). MS made of P(DL)LA polymer (polymer chains consisting of a random distribution of enantiometers) were probed by X-Ray Diffraction (XRD) and Differential Scanning Calorimetry (DSC) as well. XRD and DSC showed no crystallinity of the PDLLA MS, in agreement with previously published studies. However, VSFG spectra and scattering patterns demonstrate that there is still a finite number of crystallites with maximum extension of 250 nm (radii). This indicates VSFG has an increase in sensitivity that is roughly 2 orders of magnitude more than XRD.[3] This opens up new possibilities in the description of early stages of nucleation and growth phenomena and possible new phases.

[1] S Roke et al. Vibrational Sum Frequency Scattering from a Submicron Suspension. Phys. Rev. Lett. 91, 2003, 258302.

[2] AGF de Beer et al. Molecular and microscopic properties of buried microstructures. Submitted.

[3] HB de Aguiar and S Roke. Sum-Frequency Generation Scattering: a higher sensitivity probe for crystalline properties. In preparation.

**BI-TuP9 Effect of Film Fabrication Method on the Protein Fouling Resistance of Mixed Oligo(ethylene glycol) Films**, ***J.A. Ruemmele**, M.S. Golden, R.M. Georgiadis*, Boston University

A major concern in the design of biosensors for studying protein interactions is protein fouling, or non-specific binding, which masks the signal from the binding event of interest. Mixed oligo(ethylene glycol) (OEG) films have become a standard surface coating used to avoid fouling of gold sensor surfaces. Such films comprise a probe coupling OEG (A) and a diluent of protein resistant OEG (B). Two methods exist for the fabrication of such surfaces: co-deposition of A and B, and sequential deposition, where A is inserted into a pre-existing monolayer of B. Though films fabricated by sequential deposition display better fouling resistance, the source of this resistance is unclear. It has been hypothesized that the improved fouling resistance is due to an absence of islanding in the film, however it could simply result from an extremely low A content. In order to identify the affect of the fabrication method, films prepared by both approaches must contain the same amount of A. Since few techniques exist which can accurately measure low amounts of A attached to a surface, the amount of probe which covalently couples to a film was used to evaluate the film's A content. Using this technique, the fabrication conditions for both methods were adjusted to produce films containing the same amount of A. The extent of fibrinogen fouling on these now comparable films was measured with surface plasmon resonance imaging to evaluate if the actual fabrication method affects a film's fouling resistance. Furthermore, electrochemically induced reductive desorption was used to indicate any presence of islanding and to evaluate film stability.

**BI-TuP10 Specific versus Non-Specific Protein Adsorption: Effects of Chain Length and Tailgroup in Functionalized Poly(ethylene glycol)-Terminated Self-Assembled Monolayers**, *P. Buecker, M. Himmelhaus, **R. Dahint***, University of Heidelberg, Germany

In recent years, substantial efforts have been made to develop surface coatings which limit or even suppress non-specific adsorption of proteins. While for many technological applications the surfaces are designed to exclusively repel proteins, an even more complex situation exists in biomedical analysis, where immobilized probe molecules, e.g. antibodies, are used to specifically bind target proteins from solution. Here, the coating must fulfil a two-fold function: (i) effectively suppress non-specific adsorption processes, which may both result in false interpretation of binding events and significantly lower the detection limit of the analytical techniques, and (ii) additionally facilitate the integration of the probe molecules without loss of non-specific protein repulsion. Hereby the question arises, to what extent efficient immobilization of probe molecules and suppression of non-specific interactions can actually be achieved with a single material as the repulsion mechanism inhibiting non-specific adsorption of biomolecules might also compromise the integration of the probes. In a recent study we have shown that COOH-functionalized poly(ethylene glycol) (PEG) alkanethiolate self-assembled monolayers (SAMs) $[\mathrm{HS}\text{-}(\mathrm{CH_2})_{11}\text{-}(\mathrm{OCH_2CH_2})_n\text{-}\mathrm{COOH}]$ with a mean number, n, of 33 EG units suppress non-specific protein adsorption while facilitating covalent coupling of antibodies via the terminal COOH-group.[1] We now synthesized the same type of molecule with various EG chain lengths (n = 13-40) and different tailgroups (-OH, $-\mathrm{NH_2}$, and -COOH), and compared both the antigen binding capacity and the protein resistance of the corresponding SAMs by ellipsometry, X-ray photoelectron spectroscopy (XPS), infrared spectroscopy (FT-IRRAS), and enzyme-linked immunosorbent assays (ELISA). It is observed that protein repulsion depends on the tailgroup selected and increases with increasing EG chain length. In parallel, however, the maximum amount of probe molecules that can be coupled to the films significantly decreases with enhanced EG content, thus, reducing the antigen binding capacity of the films. The results, therefore, show that for bioanalytical applications the number of EG units has to be properly adjusted in order to obtain an optimum signal-to-noise-ratio. The best performance has been observed for a chain length of about 30 EG moieties.

[1] S. Herrwerth et al., Langmuir 2003, 19, 1880.

**BI-TuP11 Quantitative Analysis of Angular Resolved XPS-Measurements: Influence of Inaccuracies in Take-Off and Acceptance Angle**, ***C. Van der Marel**, J.H.M. Snijders, D.D.C.A. Van Oers, E.P. Naburgh*, Philips Research - MiPlaza, The Netherlands

For quantitative analysis of Angular Resolved XPS-measurements the take-off angle of the detected electrons is an important input parameter. A device has been developed that allows measurement of the real take-off angle as a function of the tilt angle of the sample. The acceptance angle of the detector is also determined using this device. The device has been tested extensively in two commercial XPS-instruments (Quantera from ULVAC – PHI); small but significant deviations have been found between real and set values of the take-off angles. To investigate the influence of the acceptance angle and of inaccuracies in the take-off angles several series of samples were analyzed. The samples consisted of a homogeneous substrate coated with a thin organic layer (e.g. phosphonic SAM-layers on Al2O3, alkyl-thiols on copper). Quantitative analysis of the XPS-results provided values for the layer thickness of the organic layer, for the coverage and for the "real" atomic concentrations in substrate and in the organic layer. In the lecture it will be shown that the use of accurate values of the acceptance and the take-off angles is a prerequisite to obtain consistent results.

**BI-TuP12 Improved Osseointegration of a Novel, Hydrophilic Ti Surface: Early Events**, *A. Molenberg, **S. Berner***, Institut Straumann AG, Switzerland, *F. Schwarz, M. Herten*, Heinrich Heine University, Germany, *M. de Wild, M. Wieland*, Institut Straumann AG, Switzerland

The performance of bone-related implants is strongly connected with the properties of the implant surface. Particularly surface topography and chemistry both influence initial wettability and peri-implant bone apposition of implants. Sandblasted and acid etched (SLA) titanium surfaces are initially hydrophobic due to microstructuring and adsorption of hydrocarbons and carbonates. The purpose of this study was to investigate initial hydrophilicity and to examine tissue reactions to a newly developed chemically modified implant surface called SLActive. Implantation of SLActive and SLA implants was performed bilaterally in dogs. The animals were sacrificed after a healing period of 1, 4, 7 and 14 days, respectively. Peri-implant tissue reactions were assessed in nondecalcified tissue sections using conventional histology (Toluidine blue-TB and Masson Goldner Trichrome stain-MG) and immuno¬histochemistry using monoclonal antibodies to transglutaminase II (TG) (angiogenesis) and osteocalcin (OC) (mineralization). Bone density (BD) and bone to implant contact (BIC) were assessed histomorphometrically. Immunohistochemical staining for TG revealed a direct correlation between angiogenesis and new bone formation, which was clearly identifiable after 7 days by means of increasing BD, BIC and OC values. After 14 days, SLActive surfaces seemed to be surrounded by a firmly attached mature, parallel-fibered woven bone. The study clearly reveals an enhanced bone formation for the hydrophilic SLActive surface and thus a reduced healing time.

**BI-TuP13 Solution Deposited poly(N-isopropyl acrylamide) Films Optimized for Mammalian Cell Release**, ***J.A. Reed**, M. Bore, L.K. Ista, G.P. Lopez, H.E. Canavan*, University of New Mexico

Poly(N-isopropyl acrylamide), or pNIPAM, is a smart polymer that is of great interest in the bioengineering community. Above its lower critical solution temperature (LCST), the polymer is relatively hydrophobic, and mammalian cells grown on pNIPAM-grafted surfaces act in a similar fashion as those grown on typical tissue culture polystyrene (TCPS): they proliferate into a confluent sheet. Below the LCST (i.e., room temperature) the polymer physically changes, becoming hydrophilic and swelling. Furthermore, when the temperature of the cell culture is dropped below the LCST of the polymer, the cells will detach and can be harvested for tissue engineering applications. This is in contrast to cells grown on TCPS alone, which will not detach using a temperature drop, instead requiring enzymatic digestion (via trypsin) or mechanical scraping to remove them. In this work, we present a novel, solution-based technique to generate pNIPAM surfaces from pNIPAM and tetraethyl orthosilicate (spNIPAM). The composition of the films (i.e., weight % of pNIPAM) was optimized for reversible cell adhesion by observing the thermoresponse, surface chemistry, and cell release characteristics. Characterization of the surface chemistry of the spNIPAM substrates was done using X-ray photoelectron spectroscopy (XPS), interferometry, and contact angle measurements). Characterization of the cell-releasing behavior of the spNIPAM substrates was determined by observing the ability of surfaces to release confluent bovine aortic endothelial cells (BAECs). From these results, we conclude that the fastest, most reliable release of BAECs occurred on surfaces spin coated with a solution of .35wt% pNIPAM/TEOS.

**BI-TuP14 Nanometer-scale Cell Adhesive Patches for the Control of Cellular Functions**, ***U.A. Martinez***, *T.C. Gamble, G.P. Lopez, E.L. Dirk*, The University of New Mexico

The control of cellular functions will find many applications in the development of new materials for biomedical applications such as tissue engineering. However, for this to be possible, understanding the cell-material interactions is essential. In this work, interferometric lithography was used to create nanometer-scale patterned substrates. Interferometric lithography is a method for fabricating spatially consistent periodic patterns with the use of the interference of two coherent optical beams. The interfering beams produce a standing wave that can be recorded in a photoresist making equally spaced channels. The substrate is then rotated 90° and exposed again creating photoresist pillars. After exposure, the substrates are coated with a 30 nm layer of gold, using a 3 nm layer of chromium to enhance adhesion. An acetone lift-off procedure removes the photoresist pillars, leaving uncoated patches throughout the gold-coated surface. Self-assembled monolayers are formed on the gold-coated areas using thiols of poly(ethylene glycol) [PEG], a biologically inactive molecule that inhibits protein adsorption. Fibronectin, a protein that enhances cellular adhesion, is adsorbed onto the uncoated regions rendering cell adhesive patches. A double exposure technique has also been developed to obtain a two-fold increase in the pitch while holding the same patch size. For example, a pitch of 300 nm with a 100 nm patch can be increased to a 600 nm pitch while maintaining the same size of the patch. These nanopatterned cell adhesive substrates offer a method to systematically manipulate cellular attachment to further control cellular functions such as spreading, viability and differentiation.

**BI-TuP15 Competitive Protein Adsorption to Biomaterials and the Dependence on Protein Concentration**, ***M. Holmberg***, *X. Hou*, Technical University of Denmark

Quantitative analysis of protein adsorption to artificial materials is of importance in evaluating the potential of biomaterials. Proteins have a central role in all living organisms and are present in basically all parts of the human body and the first thing to happen when an artificial material is introduced into a human body, or another biological system, is unspecific adsorption of proteins onto the surface of the material. Most studies on blood protein adsorption to polymer surfaces reported in the literature are performed from low concentration (≤1 mg/ml) single protein solutions. However, it is not evident that those results also are valid for protein adsorption from protein mixtures with high protein concentration (≥10 mg/ml). When biomaterials are introduced into a human body, thousands of different proteins, sometimes present in quite high concentrations, will come in contact with the material and there will be competitive protein adsorption on the surface of the material. By labelling proteins with different radioisotopes one can monitor the adsorption of several proteins onto surfaces simultaneously, and with this multi-labelling technique one can study competitive adsorption and use complex solutions such as human serum during adsorption experiments. Albumin and IgG (Immunoglobulin G) adsorption to both unmodified and modified PET (polyethylene terephthalate) surfaces from single protein solutions and human serum solutions has been monitored using radioactive labelling. The PET surfaces are modified through plasma polymerisation using the monomer DEGVE (diethylene glycol vinyl ether), which results in a more hydrophilic and anti-fouling surface than the PET surfaces. Results show that the detected anti-fouling quality of DEGVE surfaces is influenced by the concentration of the protein solution used. Albumin and IgG adsorption from human serum dilutions corresponding to 0.1% human serum shows that the albumin and IgG adsorption is significant lower on the DEGVE surface than on the PET surface, and that this antifouling characteristics of DEGVE surfaces can be stable for at least 24 hours. However, performing the same experiment, including the same rinsing procedure, with ≥10% human serum solutions, the detected albumin and IgG adsorption to DEGVE approaches the adsorption detected on unmodified PET. Thus, evaluation of biomaterials should be performed in an environment similar to the one the material is intended to operate in.

**BI-TuP16 Scanning Tunneling Microscopy Studies of Photoactive Yellow Protein Anchored to the Thiol Modified Au(111) Surface**, ***I.I. Rzeznicka***, RIKEN, Japan, *G.W.H. Wurpel*, Utrecht University, The Netherlands, *M. Bonn*, FOM Institute for Atomic and Molecular Physics (AMOLF), The Netherlands, *M.A. van der Horst, K. Hellingwerf*, University of Amsterdam, The Netherlands, *S. Matsunaga*, The University of Tokyo, Japan, *T. Yamada*, RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan

Adsorption of proteins on metal surfaces and their interactions present an important technological challenge in the field of biotechnology and construction of biomolecules-based functional devices. The process of protein adsorption is very complex and depends on surface properties, protein structure and its chemical composition. On Au surfaces, covalent bonding to the surface can in principle be easily achieved by utilizing unbound sulfur-containing amino acids resulting in the formation of strong Au-S bond, in analogy to the well known thiol chemistry. We studied adsorption of photoactive yellow protein (PYP) protein on Au(111) surface by scanning tunneling microscopy (STM) in air and in the electrochemical environment. The results show that cysteine-containing mutant of PYP does not adsorb on the bare Au(111) surface. Stable, densely packed protein layers were observed after protein immobilization via amide bond formation onto self-assembled monolayers (SAMs), consisting of 3-mercaptopropanoic acid (3-MPA) and 11-mercaptoudecanoic acid (11-MUA) with the use of carbodiimide and N-hydroxysuccinimide. Layers of PYP prepared in this way show fluorescence activity visualized by fluorescence microscopy, indicating that the protein retains its photoactive function upon adsorption. We will also present our attempts to detect a photocurrent generated by laser illumination of PYP layers.

**BI-TuP17 Fabrication of Micro-Templates for the Control of Bacterial Immobilization**, ***Y. Miyahara***, *N. Saito, O. Takai*, Nagoya University, Japan

Well-defined micro-patterns of bacteria are significant as a fundamental technique for biosensor arrays utilizing rapid detection of infectious diseases and toxic compounds. Many researchers have studied control methods to fabricate the micro-patterns. However, in these researches, many processes are required for the immobilization and the regioselectivity is not so good. In this study, we aim to fabricate well-defined micro-patterns of bacteria using two types of micro-patterned templates and to elucidate the adhesion behaviors of several bacteria onto the templates from viewpoint of surface topology and chemical properties. Super-hydrophobic/super-hydrophilic and super-hydrophobic/polyethylene glycol (PEG) micro-patterns were fabricated as the templates. In the case of super-hydrophobic/super-hydrophilic patterns, the difference of surface energy in the respective regions differs greatly. The difference could have a great effect on the adhesion of bacterial. In the case of super-hydrophobic/PEG micro-patterns, PEG surface generally avoid the adhesion of bacteria due to volume exclusion effect of PEG based on the structural fluctuation. Super-hydrophobic surface was prepared by microwave plasma enhanced chemical vapor deposition (MPECVD) from trimethylmethoxysilane (TMMOS). Super-hydrophobic/super-hydrophilic micro-patterns were fabricated by irradiating the super-hydrophobic surface with vacuum ultra violet (VUV) light through a stencil mask. In the case of Super-Hydrophobic/PEG micro-patterned surfaces, PEG surfaces were fabricated by reacting COOH groups of methoxypolyethylene glycol propionic acid with $NH_2$ groups of $NH_2$-terminated self assembled monolayer in ion-exchanged water. The super-hydrophobic regions were fabricated by MPECVD thorough a stencil mask. Bacteria were cultured on the respective templates in the incubator controlled under the $CO_2$ concentaration of 5 % at 37 $^{o}$C. After culture, bacteria were observed by phase-contrast microscope. The surfaces were characterized by XPS and FT-IR. As a result, in the case of super-hydrophobic/super-hydrophilic micro-patterns, some bacteria (Escherichia coli, Bacillus subtilis) were adhered to only super-hydrophobic regions. But others bacteria (Pseudomonas stutzeri, Pseudomonas aeruginosa) were not separated well. Their results attribute bacterial charge, cell division rate and adhesion time lag between super-hydrophobic regions and super-hydrophilic regions.

**BI-TuP18 Kinetic Study on Protein Adsorption on Polyelectrolyte Brush Surface**, ***H. Tatematsu***, Nagoya University, Japan, *T. Fujima*, Musashi Institute of Technology, Japan, *N. Saito, O. Takai*, Nagoya University, Japan

Polymer chains grafted in the high density stretch perpendicularly by repulsive interaction. This is a so-called brush. The various functional groups can be also introduced into polymer brush as lateral chains. The 3-dimensional structure was varied by the type of lateral chains. On spherical polyelectrolyte brush (PEB), strong adsorption of protein takes place at low ionic strength whereas less protein is adsorbed at the high ionic strength.[1] In addition, protein structure and character remain via adsorption.[2] These properties can be applied to improvement of biocompatibility and Drug Delivery System (DDS). However, the kinetics of adsorption on normal PEB surface has not been understood well. Thus, in this study, we aimed to investigate the kinetics of protein adsorption on PEB. Polystyrene brush (PSB) surface was fabricated by reacting polystyrene terminated by a trichlorosilane ($PS\text{-}Cl_3$) group with silanol (Si-OH) groups on the silicon wafer. PSB brush was converted to polystyrene sulfonate sodium salt brush (PSSB) by sulfonation and neutralization. In protein adsorption experiment, the solution of Bovine Serum Albumine (BSA) in phosphate buffer saline (PBS) was used. NaCl aqueous solution adjusted to various concentrations was added to the stock solution in order to extract the effect of ionic strength. Protein adsorption was evaluated by Fourier transform infrared spectroscopy (FT-IR) and the evanescent adsorption spectroscopy (EOS). The proteins on the surfaces were observed by atomic force microscope

(AFM). Relationship between the amount of adsorption and the ion strength on normal PSSB surface differs from that on spherical PSSB surface in previous reports. This would originate from structural configuration of PEB. Finally, we propose a kinetic model of the adsorption on PSSB based on the variation of adsorption against time and ion strength by FT-IR, EOS and AFM.

[1] A. Wittemann and M. Ballauff, Phys. Chem. Chem. Phys., 2006, 8, 5269-5275

[2] B. Haupt, Th. Neumann, A. Wittemann, and M. Ballauff, Biomacromolecules 2005, 6, 948-955

**BI-TuP19 Surface Characterization of PEG-like Film Made by Using Ethylene Glycol Precursor and Capacitively Coupled Plasma Chemical Vapor Deposition***, C. Choi, S. Lee, D. Jung,* Sungkyunkwan University, Korea*, D.W. Moon, T.G. Lee*, Korea Research Institute of Standards and Science (KRISS)

Polyethylene-glycol (PEG) is widely used for various biological applications because of its anti-fouling property for protein and cells, and non-toxicity in the human body. Since the PEG thin film should have the properties of reproducibility and adhesiveness on various substrates, in this work, plasma-polymerized ethylene glycol (PPEG) thin film was deposited on a glass surface by using the capacitively coupled plasma chemical vapor deposition (CCP-CVD) method and ethylene glycol as a precursor. The PPEG thin films were characterized by using contact angle measurement, X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (TOF-SIMS) along with a principal component analysis (PCA). The PPEG surface was controlled in a reproducible manner as a function of sample bias plasma power and was correlated with the surface chemical composition. Of interest, we found that PPEG thin film surfaces deposited at low plasma power were similar in chemical composition to the PEG polymer surface. In addition, by using the fluorescence detection method, we found that the PPEG surface showed an anti-fouling property of immunoglobulin G protein, which was tagged by fluorescein isothiocyanate. Our results showed that this PEG-like PPEG surface would be useful for protein chip applications.

**BI-TuP20 Determination of Standard-State Adsorption Free Energy for Peptide-Surface Interactions by SPR Spectroscopy without Peptide-Peptide Interaction Effects***, **R.A. Latour**, Y. Wei*, Clemson University

As an approach to gaining fundamental insights into the thermodynamics of protein-surface interactions, we are quantitatively determining the standard state free energy of peptide-surface interactions using a host-guest peptide model in the form of TGTG-X-GTGT, where the T (threonine) and G (glycine) flanking sequences are the host residues and X represents a variable guest residue. Alkanethiol self-assembled monolayers (SAMs) with a broad range of polymer-like functionalities are being used as the adsorbent surfaces. With this experimental model, we are able to determine contributions of individual mid-chain amino acid residues on peptide adsorption behavior. The most common way of determining the standard state free energy of adsorption of a peptide to a surface is by use of the Langmuir equation fitted to an adsorption isotherm. This method, however, has the inherent problem of the influence of peptide-peptide interactions at the interface. These effects can substantially affect the shape of the isotherm, leading to errors in the calculated values of the standard state free energy of adsorption. We have developed a new approach to solve this problem and provide accurate, quantitative measurements of the standard state adsorption free energy using surface plasmon resonance (SPR) spectroscopy based on chemical potential relationships vs. the classical Langmuir equation. In addition, we have also developed a very simple, automated method of accounting for bulk shift effects, which can be problematic when doing SPR adsorption studies. These novel methods will be presented along with results for a series of peptide adsorption systems using these methods.

## BioMEMS Topical Conference
## Room: Hall D - Session BM-TuP

## BioMEMS

**BM-TuP1 Electrowetting Using Probe of Atomic Force Microscope as Mobile Electrode***, **X. Ling**, B. Bhushan*, The Ohio State University

The wetting behavior of liquid droplet on nanostructured surface can be dynamically tuned using electrowetting technique. A conductive AFM probe is used as a mobile electrode to replace the normally fixed electrode in conventional electrowetting setup. The forces involved in the electrowetting process are quantitatively measured from the deflection of AFM cantilever. The AFM tip geometry is precisely determined using SEM and calibration standard. The force between the AFM tip and the droplet is modeled and quantitatively compared with experimental results. By actuating the AFM probe vertically and laterally using the integrated piezo-driver, the droplet is actuated on the nanostructured surface in a fully controllable way due to the capillary force between the AFM tip and the droplet. The actuated droplet is used as a nano-vehicle to effectively transport and/or arrange other nano-objects on surface with capillary-induced manipulation, which opens a new way to integrate nanometer-sized building-blocks that were not movable with other methods.

**BM-TuP2 Nanoscale Adhesion, Friction and Wear Studies of Biomolecules on SAM-Coated Silicon Based Surfaces***, B. Bhushan, **K.J. Kwak**, S. Gupta, S. Lee*, The Ohio State University

Protein layers are deployed over the surfaces of microdevices such as bioMEMS and bioimplants as functional layers that confer specific molecular recognition or binding properties or to facilitate biocompatibility with biological tissue. When a microdevice comes in contact with any exterior environment, like tissues and/or fluids with a variable pH, the biomolecules on its surface may get abraded. Silicon based bioMEMS are an important class of devices. Adhesion, friction and wear properties of biomolecules (e.g., proteins) on SAM coated silicon based surfaces are therefore important. These studies have been carried out on protein biomolecules using tapping mode AFM. Based on this study, adhesion, friction and wear mechanisms of biomolecules on SAM-coated silicon based surfaces are discussed.

**BM-TuP3 Measurement of the Slip Length of Water Flow on Hydrophilic, Hydrophobic and Superhydrophobic Surfaces***, Y. Wang, **B. Bhushan***, The Ohio State University

The growing interest of boundary slip at liquid-solid interface in micro/nano scale is an important issue in microfluidics systems, where lower liquid flow friction is generally desirable. Recent studies have shown that the no-slip boundary condition is not always valid on micro/nano scale, especially on hydrophobic. Theoretical and experimental studies suggest that at the liquid-solid interface, the presence of gas bubbles is responsible for the breakdown of the no-slip condition for hydrophobic surfaces. The degree of boundary slip at liquid-solid interfaces is usually quantified by a parameter called slip length, which infers a distance between a liquid-solid interface and a virtual no-slip interface. Atomic force microscopy is a powerful tool to measure slip length. It has also been used to image nanobubbles in tapping mode. Although the slip length has been reported on both hydrophilic and hydrophobic surfaces, the direct experiment evidence has not been given between nanobubble and apparent slip on hydrophobic surfaces, as well as the relationship between bubbles' properties and slip length. In this study, the colloidal probe techniques is used to measure hydrodynamic force on hydrophilic, hydrophobic and superhydrophobic surfaces with AFM. The slip length is obtained based on a model proposed in the literature. By combining nanobubble images on hydrophobic and superphdrophobic surfaces, the contribution of nanobubbles to boundary slip is studied with known bubble properties, such as size and distribution density. A model is presented for nanobubbles' friction reducing mechanisms.

**BM-TuP4 Electrical Assay for Real-Time Monitoring Cardiomyocyte Apoptosis***, **Y. Qiu**, X. Zhang*, Boston University

Deregulated cardiomyocyte apoptosis is a critical risk factor in a variety of cardiovascular diseases. Though enzymatic DNA fragmentation is most commonly used criteria of apoptosis at the level of individual cardiomyocytes, the capability of detecting cell detachment will provide instant information at early phase of apoptosis. Furthermore, the assays used to detect DNA fragmentation are all invasive to living cells, which disables real-time monitoring of the whole process. In this work, we developed an impedance-sensing assay for real time monitoring cardiomyocyte apoptosis induced by tumor necrosis factor alpha (TNF-alpha) based on recording the change in cardiomyocyte adhesion to extracellular matrix (ECM). Electrochemical impedance spectroscopy (EIS) was employed in impedance to process the impedance spectra, followed by manual calibration with electrical cell-substrate impedance sensing (ECIS) technique. Adhesion profile of cardiomyocytes undergoing cell death process was recorded in a time course of equivalent cell-substrate distance. Multiple concentration levels of TNF-alpha (from 10 to 80 ng/mL) were applied to the cultured cardiomyocytes and the concentration-related adhesion profiles were recorded for the cell death process. An optimal concentration of TNF-alpha (20 ng/mL) was determined to induce cardiomyocyte apoptosis rather than necrosis because of its mild slope of developing cell detachment in 24-hour real-time monitoring. It was also observed in the Trypan blue exclusion (TBE) results that a gradual and significant increment in cell death rate was achieved with a concentration level of 20 ng/mL. Treat with optimal concentration of TNF-alpha, the cardiomyocytes first experienced a transient drop in cell-substrate distance followed a sustained cell detachment. The equivalent cell-substrate distance increased from 59.1 to 89.2 nm within 24 hours. The early change of cell adhesion was proven related to cardiomyocyte apoptosis with the following TUNEL test in which the treated cardiomyocytes suffered an apoptotic percentage of 21.1 ± 5.5 % (vs. 5.9 ± 2.5 % in the control sample). This novel assay has the potential to become a valuable high-throughput experimental approach in studying in vitro cardiomyocyte apoptosis research.

**BM-TuP5 Parylene Electrothermal Valves for Rapid In Vivo Drug Delivery*, P.-Y. Li,*** *D.P. Holschneider, J.-M.I. Maarek, E. Meng*, University of Southern California

Two single-use electrothermal valves featuring low power (mW) and rapid operation (ms) were designed, modeled, fabricated, and tested. They share a common layout consisting of a composite membrane (Parylene/Pt/Parylene) situated in the flow path between two catheter segments. Current applied to the Pt thermal element initiates Joule heating that leads to thermal degradation or melting of the membrane and causes the valve to open. Compared to previous work employing metal membranes, Parylene enables low power operation (thermally degraded (125-200°C) or melted (290°C) at much lower temperatures). Parylene also enables large robust membranes for larger effective valve opening area (in this case, 330-500 μm). Membrane designs were mechanically modeled to assess performance using a large deflection (Parylene only) and nonlinear FEM models (composite). The nonlinear model indicates 1.53GPa maximum stress of the Pt element under 1 atm pressure (peak under normal operation) which is less than its tensile strength (1.83GPa); modeling and load deflection experiments showed good agreement. Transient thermal FEM modeling and video microscopy were used to investigate thermal events leading to valve opening; simulation and experimental results were in close agreement. The temperature coefficient of resistivity of the Pt element and the resistance change as a function of applied current were obtained. These results allowed prediction of the temperature of the Pt thermal element and determination of the appropriate operating current. For the prototype valve having a serpentine Pt element spanning the valve area, 25-50 mW was required to open the valve under constant current operation in air and a current ramping rate of 0.1 mA/sec was the optimal condition for valve opening for use with water. The best opening time achieved with this design was 100 ms in air but several seconds in water. The optimized valve further improves the opening speed; the Pt element (straight and serpentine) was defined only at the perimeter of the valve except for a small gap where the element connects to contact pads. Preliminary results indicate that the optimized valve can be opened in water in the millisecond range (100 mW). We also demonstrate successful application of our valve in a wirelessly operated minipump that allows bolus drug infusion in animals.

**BM-TuP6 Mapping Smooth Muscle Cell Contractile State Regulated by Contractile Proteins using a Novel BioMEMS Moire Mapping Sensor*, X.Y. Zheng,*** *X. Zhang*, Boston University

Abnormal vascular smooth muscle cell contractility plays an important role in the pathogenesis of hypertension, blood vessel spasm, and atherosclerosis. This paper presents the mapping of smooth muscle cell contractility using a novel optical moiré method. We utilized coherent laser beams to illuminate periodic polymeric substrates where isolated cells were cultured. The diffraction phenomena of coherent laser beams through the polymeric periodic substrates where living cells were cultured introduces moiré patterns and can be used to real-time mapping the cell-substrate traction forces. The PDMS micropillar arrays were embedded between large sidewalls for cell guidance. A polycarbonate flow perfusion chamber is sealed under the chip. The same chip with imbedded pillars with aspect ratio of 1:3 was mounted on a rotational stage parallel to the first substrate. Diffraction moiré patterns can be generated by illuminating coherent beam via two parallel grating lines or grids. The grating lines served as reference gratings for diffraction moiré pattern generation in (0,1,0) or (1,0,0) direction whereas two-dimensional moiré fringes can be formed via two paralleled imbedded pillars. Therefore, contraction of the vascular smooth muscle cells can be real time "magnified" and "mapped" through moiré pattern evolutions. For contractility mapping of vascular smooth muscle cells, we considered the cell total area, cell length and width. On the other hand, we measured the distortion area of the moiré patterns, moiré pattern length and width. In the experiment, these two factors were shown to be consistent. Further, vascular smooth muscle cells were cultured on substrates with serum media to develop focal adhesion, and then the cells were relaxed on serum free media for another 48 hours followed by treating SMCs with contractile agonist lysophosphatidic Acid. We found that the area of the distorted moiré patterns produced on two overlapped periodic substrates were inversely correlated with the distortion of the moiré patterns, thereby indicating that the contraction of vascular smooth muscle cells were inversely correlated with the initial spreading developed in serum. We anticipate that this method will increasingly provide more applications and cell biological insights in vascular cell contraction mechanism study.

**BM-TuP7 Toward a Selective Optical Biosensor for Integrated Biofilm Detection*, M.T. Meyer*,** *S.T. Koev, R. Fernandes, W.E. Bentley, R. Ghodssi*, University of Maryland

Certain types of bacteria regulate gene expression through quorum-sensing, the detection of extracellular levels of bacterial signaling compounds. Once bacteria sense their population is sufficiently large to overwhelm a host's immune system, they will aggregate and form a pathogenic matrix of bacteria, or biofilm. While this phenomenon is not fully understood, it is of interest to study biofilms to gain knowledge toward developing new antibacterial treatments. We have developed a platform for examining bacterial biofilm growth and response in a microfluidic environment using optical monitoring of selectively deposited Escherichia coli. Bacterial growth over time was quantified via optical absorbance using an external photodiode; the use of an optical sensor isolated from the fluidic environment allows for more reliable sensor operation as well as increased sensitivity. Two bacterial adhesion layers were investigated, including the amino-polysaccharide chitosan and a fusion protein (E72G3), consisting of a hydrophobic domain and an antibody-binding protein G domain, bound to antibodies against E. coli. E. coli cells were immobilized on electrodeposited chitosan, and biofilms were grown over a period of 48 hours. While chitosan can be selectively deposited and promotes bacterial adhesion, results show that material irregularities impede optical observation of the progression of biofilm growth. E72G3 was also used to immobilize E. coli by depositing the proteins on a patterned hydrophobic surface, then immobilizing antibodies against E. coli on E72G3. This method of bacterial deposition can be extended to numerous other pathogens by virtue of the fusion protein's antibody-binding properties. Optically detectable biofilm formation was confirmed on this spatially and biologically selective surface. The platform can be used to quantify normal biofilm formation in addition to biofilm formation in response to external stimuli. Detailed device fabrication and testing parameters as well as experimental results will be presented. Our goal is to develop this platform into a fully integrated, compact device with highly parallel throughput for applications in discovering new antibacterial agents.

**BM-TuP8 In-vitro Comparison of Activated and Sputtered Iridium Oxide Neural Microelectrodes*, S. Negi,*** *R. Bhandari, L. Rieth, R.A. Normann, F. Solzbacher*, University of Utah

To provide low impedance electrical connection between the neural electrode and the nerve, the electrodes are coated with conductive material like Iridium oxide (IrO$_x$) due to its higher charge injection capacity and resistance to corrosion.[1] In this report, IrO$_x$ is deposited by two methods; activation of iridium to form activated iridium oxide film (AIROF), and reactive sputtering to form sputtered iridium oxide film (SIROF) on similar shape and size neural electrodes. The AIROF and SIROF properties are studied and the results are compared. Utah Electrode Arrays (UEAs), were used for this study.[2] To fabricate AIROF coated UEA, 99.8 % pure Ir was DC sputter deposited on to the UEA tips using an Ar pressure of 20 mTorr, and 5W power for 12 minutes to achieve 1000 Å thickness. The Ir electrodes were activated by cyclic voltammetry (CV), sweeping between -0.8 to +0.8 V versus Ag/AgCl in phosphate buffered saline (PBS) solution at the rate of 1 Hz. The SIROF films were deposited on the UEA tips by pulsed-DC reactive sputtering with 50%:50% ratio of Ar and O$_2$ in the ambient, keeping the chamber pressure at 10 mTorr. Ar and O$_2$ flow rates were both 100 sccm. The pulse frequency was at 100 kHz, the duty-cycle was 30 percent, and a power of 100 W was used to achieve thickness of 1000 Å after 20 minutes of deposition. Charge storage capacity for AIROF and SIROF coated UEAs was found to be 10 and 38 mC/cm$^2$, respectively. The electrochemical impedance at 1 kHz was measured for AIROF and SIROF as a function of the exposed UEA tip. At 100 μm tip exposure, AIROF and SIROF impedance were 36 and 6 kΩ respectively, while, at 20 μm tip exposure the AIROF and SIROF impedance were 200 and 50 kΩ respectively. The results indicate that decreasing the tip exposures increases impedance exponentially. SIROF coated electrodes have lower impedance and, potentially, will offer higher neural selectivity without compromising on the electrode sensitivity. The higher charge storage capacity and lower impedance makes SIROF a promising material for stimulating and recording neural signals.

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[2] K. E. Jones, P. K. Campbell, and R. A. Normann, A glass/silicon composite intracortical electrode array, Ann. Biomed. Eng., vol. 20, no., pp 423-37, 1992.

**BM-TuP9 Capillary Electrophoresis Electrochemical Detector using Capacitometric Method for Endocrine Disruptor Detection*, J.W. Yoo,*** *K. Ha, Y.S. Kim, C.J. Kang, Y.J. Choi*, Myongji University, Korea

Interests in the use of polymeric materials such as polydimethylsiloxane (PDMS) and polymethylmethacrylate (PMMA) have increased over the past few years. PDMS has been widely discussed due to fine optical transparency for detection, curability at low temperatures, easily replicable molding and fine adhesion. In past, PDMS substrate based capillary electrophoresis-electrochemical detection (CE-ECD) microchips have been developed for separation and detection of endocrine disruptors. We also developed systems and measured bisphenol-A (BPA) and butylphenol as well as dopamine and catechol with various electrode structures such as ITO, Au as well as Prussian blue modified ITO and Au. Whereas, because of the sensitivity and structural dependence of measurement, capacitance based detection of these chemicals have not been attempted much so far. The strong point of the capacitometric method is that the electrode doesn't need to be contacted with a sample or electrolyte, resulting in reproducible and more reliable results than those from the amperometric detection. Thus, as long as high sensitivity of capacitance can be achieved with a suitable detection system, we can apply it to even a flowing channel system. To do that, we used a high frequency cavity resonator and measured dC/dV with a resolution of better than 10-18 F/V. A device including microchannels built using PDMS mold was also fabricated on glass substrate. In this work, we studied capacitometric detection of BPA. The separation of BPA was carried out using a 7 cm long capillary. A solution containing MES of pH 6.5 was used as separation buffer. A field of 60 V/cm was applied to a channel for separation and the same field for injection for 10 seconds. With a time evolutional monitoring of dC/dV, 100 μM to 10 mM BPA could be detected.

**BM-TuP11 Microcantilever Grafted with Responsive Polymer Brushes for Glucose Sensing**, ***T. Chen***, Duke University, *R. Desikan, R.H. Datar, R.P. D, T.G. Thundat,* Oak Ridge National Laboratory, *S. Zauscher*, Duke University

There is considerable interest in microcantilevers grafted with stimulus-responsive polymer brushes for sensor applications in aqueous environments, as they potentially provide a much larger cantilever bending response to changes in stimuli, such as temperature, light, chemical, and pH compared with cantilevers decorated with self-assembled monolayers (SAMs). To engineer sensitivity to specific stimuli, functional monomers can be incorporated into polymer brushes via copolymerization and functional moieties can be introduced through subsequent chemical modification. As boronic acid can bind diols through reversible boronate ester formation, incorporation of boronic acid into linear copolymers such as latex and polymer gels for the detection of glucose has been shown. Herein, we show the synthesis of novel glucose-responsive poly(N-isopropylacrylamide)-co-poly(acrylic acid)-(3-aminophenylboronic acid) (pNIPAAM-co-pAA-PBA) polymer brushes, and explore their use in a prototypical example for their potential as polymer brushes-functionalized microcantilevers firstly for the detection of blood glucose at physiologically relevant concentrations. We evaluated the stimulus-response of the polymer brushes to changes in glucose concentration and solution pH by measuring concomitant brush height changes. Glucose-responsive pNIPAAM-co-pAA-PBA brushes show a large, reversible swelling response in presence of free glucose at physiologically relevant concentrations. The deflection and surface-stress response of microcantilevers, functionalized with PBA-brushes, is substantially larger and faster than that for PBA-SAM functionalized levers. This shows the promise of pNIPAAM-co-pAA-PBA brushes for microcantilever glucose sensing applications, and demonstrates, more generally, the potential of responsive polymer brushes to sense and transduce changes in a solution environment efficiently.

## Biological, Organic, and Soft Materials Focus Topic
## Room: Hall D - Session BO-TuP

## Biological, Organic, and Soft Materials Focus Topic Poster Session

**BO-TuP1 Photoluminescence Characterization of Highly-Functional Molecule Doped Polythiophene Films Modified by Donor and Acceptor Molecules**, ***H. Kato***, *S. Takemura, H. Kobe, Y. Mori, Y. Matsuoka, K. Shimada, T. Hiramatsu, N. Nanba, K. Matsui*, Kanto Gakuin University, Japan

Conducting polymer polythiophene (PT) films incorporated with highly-functional molecules such as copper phthalocyanine (CuPc), fullerene C60, and rhodamine B (RB) were synthesized and characterized by photoluminescence measurements in order to fabricate organic hybrid materials with optical emission properties. The changes in photoluminescent properties of the hybrid polymer materials were investigated in the presence of electric field during the synthesis. The affection to the photoluminescence properties by donor and acceptor molecules such as tetrathiafulvalene (TTF) and tetracyanoquinodimethane (TCNQ) were also investigated. The electrochemical polymerization was performed in acetonitrile containing thiophene monomer and (Et)4NBF4 as a supporting electrolyte and the polymerization on an indium tin oxide (ITO) was conducted by applying positive voltage to the anode. The molecule doping in the polymer film was performed by electrochemical and diffusion methods. Photoluminescence emission peak was observed at 594 nm in the case of PT doped sample with CuPc by diffusion method. The emission peak was observed at 540 nm shifted to the lower wavelength in the case of electrochemically positive voltage applied sample after CuPc was diffused into the PT. Adding C60 molecules to the CuPc diffused PT sample by the diffusion method made the emission peak shift to the higher wavelength at 730 nm suggesting the molecular interaction between CuPc and C60 in the photoluminescence emission process because double emission peaks were observed at 590 and 735 nm in the case of single doping of C60. In the case of single doping of C60, successive electrochemical process made the double emission peaks single peak at 580 nm. TTF and TCNQ adding to the hybrid polymer films caused peak shift, peak loss and enhancement. In the case of RB diffused PT sample, photoluminescence peak at 590 nm was observed. Electrochemical process made the photoluminescence peak shift which depended on the applied voltage. Adding TCNQ to the RB diffused PT caused the enhancement of the emission peak. The present work clarified that the photoluminescence emission peak position was varied and controlled by electrochemically applying voltage or adding donor and acceptor molecules. This work was supported by High-Tech Research Center Project aided by MEXT.

**BO-TuP2 Structured Polyelectrolyte Surfaces: Tunable Surface Morphology and its Influence on Biofouling**, ***X. Cao***, *F. Wode, A. Rosenhahn, M. Grunze*, University of Heidelberg, Germany, *J. Fu, J. Ji, J. Shen,* Zhejiang University, P.R. China, *F. Leisten,* University of Hannover, Germany, *R. Mutton, C. Sheelagh, A. Clare,* University of Newcastle, UK, *M. Pettitt, M. Callow*, University of Birmingham, UK

In the search for new coatings to protect surfaces from biofouling in marine environments the surface morphology is one important variable. In order to study the influence of different structure sizes, bioinspired polyelectrolyte multilayer coatings were applied and their effect on the settlement of Ulva linza zoospores and Barnacle cyprids was studied. The multilayers were constructed by the deposition of oppositely charged polyelectrolytes through layer-by-layer deposition. Hierarchical surface structures with different texture sizes and roughnesses were obtained by adjusting the preparation conditions. Surface characterization was carried out by contact angle measurement, spectral ellipsometry, X-ray photoelectron spectroscopy, scanning electron microscopy, atomic force microscopy and confocal microscopy to quantify wetting properties, coverage, chemistry, lateral size and aspect ratio of the topographical features. We discuss how variation of the salt concentration changes resulting morphologies. Settlement of Ulva spores and Barnacle cyprids was significantly affected by texture size and roughness. We compare the effect of topography on biofouling with the surface properties and the contact area for the different organisms. Surface modifications with fluorinated silane and poly(ethylene glycol) (PEG) combine the effects of chemistry and topography. Fluorinated, hydrophobic multilayers exhibited higher settlement than the uncoated polyelectrolyte surfaces for Ulva and reduced settlement for barnacle cyprids, while for PEG coated hydrophilic surfaces the anti-fouling performance was drastically enhanced.

**BO-TuP3 Characterization and 3D Numerical Modeling of a UV/Ozone Duplex Sterilizer**, ***J.E. Jee***, *W.K. Yang, J.H. Joo*, Kunsan National University, Korea

We investigated sterilization characteristics of UV lights by counting the number of bacteria units with varying sterilization time and distance from the light source. When we irradiated 253.7nm on pens, we used UV transparent quartz plate as a support and put a reflecting plate and UV effect is increased about twice. But even with an Al reflector, multi-layered pens could not be treated properly from UV irradiation only. So, we focused on an idea that UV light of 184.9nm could generate ozone and developed a new sterilizer. Ozone generating lamp could treat more uniformly multi-layered pens with a stirring fan by supplying ozone to shadowed surfaces and keep out the temperature rising. Distribution of UV irradiation intensity and ozone supply were analyzed by a 3D model with varying geometry, position of reflectors and fans and confirmed by a semiconductor UV sensor and ozone analyser. We tried to evaluate the enhancement of a $TiO_2$ photo-catalytic surface by direct sampling with a differentially pumped QMS.

**BO-TuP5 Time-of-Flight Secondary Ion Mass Spectrometric (ToF-SIMS) Analysis for the Study of the Tertiary Structure of Polysiloxanes in Monolayer Films, Blends and Copolymers**, ***H.K. Moon***, *J.A. Gardella*, University at Buffalo

Time of flight secondary ion mass spectrometry (TOF-SIMS) is a powerful technique that can be used to investigate the conformation at the surface of a polymer film. Since the late 1990's TOF-SIMS studies of polymer tertiary structure have been reported for only a few polymers.[1-4] In this study, poly(methylphenylsiloxane) (PMPhS) is studied as another candidate polymer. The films which have the different conformations were manufactured by using Langmuir technique and solution cast method. For these different films, the difference of the fragment ion clusters in the high mass range of TOF-SIMS spectrum was investigated and additionally, reflection-absorption Fourier transform infrared spectroscopy (RA-FTIR) was used to confirm the result of ToF-SIMS. However, previous ToF-SIMS studies of tertiary structures of the polymers at their surface have been limited to the fundamental Langmuir model system.[1-4] Thus, the tertiary structure of poly(dimethylsiloxane) (PDMS) in a more realistic model will be investigated by using ToF-SIMS. First, the tertiary conformations of PDMS monolayers on a polystyrene (PS) substrate, as determined from high mass fragment intensity ratios[4] are determined. Then, the conformations of PDMS blocks, in a PS-PDMS-PS block copolymer, segregated at the surface of blends of PDMS-PS block copolymer and PS homopolymer are determined.[5] Thus, the PDMS film on the PS substrate can be regarded to the intermediate model between PDMS in the fundamental Langmuir film and PDMS segregated at the surface of a PDMS/PS copolymer or blend film.

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**BO-TuP6 Partitioning Fracture Energy of a Molecularly Tailored Interface: Bond Cleavage and Plasticity**, ***A. Jain**, Y. Zhou, S. Nayak, P. Ganesan,* Rensselaer Polytechnic Institute*, M. Lane,* Emory and Henry College*, G. Ramanath*, Rensselaer Polytechnic Institute

Separating the work of adhesion and plastic energy contributions to fracture toughness is essential to understand the mechanisms of interface debonding in thin film stacks and tailoring thin interfaces with desired properties for many applications. Here, we quantitatively separate the two contributions for Cu-silica interfaces modified with a molecular nanolayer by four-point bend testing at controlled environments to reveal the controlling mechanisms of energy dissipation. Recent work has shown that annealing Cu-silica interfaces treated with sub-nm-thick molecular nanolayers (MNLs) of a mercaptan-terminated organosilane MNL can yield manifold increase in toughness due to Cu-S bonding and thermally-activated siloxane (Si-O-Si) bridging. The increased fracture toughness, however, exceeds that of fused silica, indicating the importance of secondary absorbing processes in the Cu layer. Since Si-O-Si bridges are susceptible to hydrolysis, varying the water content provides a facile means for tuning the strength of the Si-O-Si bridges, and hence for isolating the contributions of the work of adhesion and the plastic energy. We measured interface toughness of Cu/MNL/SiO2 structures by four-point-bend testing as a function of water partial pressure pH2O under fixed displacement. In all cases, X-ray photoelectron spectroscopy measurements of the fracture surfaces indicated debonding due to siloxane bridge fissure at the MNL-SiO2 interface. The resultant plots of debond rate, V, vs. debond driving energy, G, show two distinct regimes. At pH2O < 1100 Pa, the plasticity in the Cu layer is the dominant contributor to the fracture toughness, as indicated by a high dG/d(ln pH2O), which captures the relative extents of plastic energy dissipation and work of adhesion. At pH2O > 1100 Pa, dG/d(ln pH2O) decreases by a factor of 3, due to the diminished role of large scale plasticity. Thus, our results indicate that interfacial strengthening has a multiplicative effect on the fracture toughness through a factorial contribution due to plastic energy. This result is supported quantitatively by density functional theory calculations of bond stretching in the MNL and siloxane bond breaking in the presence of water. Further, our calculations indicate water decreases the Si-O-Si bond energy by at least a third of its value in vacuum. Our results are of significance for many applications involving molecularly tailored interfaces exposed to environmental and mechanical stresses.

**BO-TuP7 Tracking of Motile Organisms by Digital In-Line Holography**, ***S. Weisse**, M. Heydt, A. Rosenhahn,* University of Heidelberg, Germany*, M. Pettitt, M. Callow, J. Callow,* The University of Birmingham, UK*, N. Heddergott, M. Engstler,* Technical University of Darmstadt, Germany*, M. Grunze*, University of Heidelberg, Germany

Digital in-line holography is based on the original idea of D. Gabor's "new microscopic principle". Using this technique an interference pattern of both the so-called "source wave" and the "object wave" is recorded which contains three dimensional information about the observation volume. Real space information about the objects can be retrieved from these holograms through application of a reconstruction algorithm. One great advantage of a holographic instrument is that focusing can be done subsequently on a computer and three dimensional information about the object of interest can be obtained. Micro-fluidic experiments and tracking algae and bacteria, have shown that moving objects can be followed in three dimensions with remarkable accuracy and high time resolution. We present two applications for this technique: understanding biofouling and following the locomotion of pathogens. The exploration behavior of zoospores of the green algae Ulva is monitored to develop a deeper insight on how biofouling occurs on surfaces. Three surfaces (glass, a fluorinated surface and a PEG2000 surface) with different antifouling performances were investigated. For these three samples full 3D motion patterns were analyzed. In the bulk water, far from the surface, spores exhibit the same motility regardless of the investigated surfaces. In close proximity to the surface motility is significantly different. The interpretation of the exploration data leads to the previously unknown conclusion that these three surfaces are colonized via a different mechanism by zoospores. A second application involves examination of the locomotion of the blood parasite Trypanosoma brucei, the causative agent of African Sleeping sickness. The self-propulsion of Trypanosoma brucei in the bloodstream of a mammalian host is an essential part of its ability to withstand the mammalian immune system. To gain deeper insights into the pathogenesis of this blood parasite, a thermo-controllable flow channel setup was developed to allow the measurement of trypanosome trajectories under physiological conditions. Measurements are carried out in a buffer solution with dextran added to mimic the viscosity of mammalian blood and with and without flow to fully characterize motility. The obtained trajectories at different ambient properties are correlated with known effects in pathogenesis.

## Energy Science and Technology Focus Topic
## Room: Hall D - Session EN-TuP

## Energy Focus Topic Poster Session

**EN-TuP1 Resistive Oxygen Gas Sensor Using Pure and Doped $CeO_2$**, ***S. Gupta***, Portland State University*, S.V.N.T. Kuchibhata, M.H. Engelhard, P. Nachimuthu, V. Shutthanandan, L.V. Saraf, S. Thevuthasan,* Pacific Northwest National Laboratory*, S. Prasad*, Portland State University

Oxygen sensors have come into wide use in automotive and industrial applications as leak detectors, industrial process flow evaluators, as well as in life science industry in diagnostic applications such as respiratory vital signs monitoring, and metabolic rate monitoring. All these applications require the fast monitoring of the oxygen gas. Hence we have explored the possibilities to develop an oxygen sensor operating on the chemiresistive principle at aggressive environments with a reduced response time. Ceria is known for its unique ability to lose or gain oxygen based on the ambient environment. The doping of trivalent elements including Y, Sm and Gd in ceria is expected to create oxygen vacancies and eventually influence virtually all types of transport properties like ionic and electronic properties. The overarching objective of this project is to study the effects of changes in surrounding conditions such as temperature, pressure, dopant concentration on the transport properties of doped ceria films. High quality, epitaxial, pure and doped ceria thin films were grown on sapphire (0001) substrates using oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and characterized them using several bulk and surface sensitive techniques. Conductivity in these films was measured as a function of temperature (room temperature to 700C) under various oxygen partial pressure (1 torr to 100 torr) and vacuum conditions. Preliminary results show that response of the doped ceria film is much faster than the pure ceria films under the same conditions of temperature and pressure. Moreover response time of these films is few milliseconds with the change in the oxygen partial pressure. It was observed that the samarium concentration of approximately 4-6 atom% is the optimum doping content.

**EN-TuP2 A Closer Look at H-CO Interaction on the Platinum Surface**, ***T. Roman**, H. Nakanishi, H. Kasai*, Osaka University, Japan

The system comprised of coadsorbed hydrogen and carbon monoxide on platinum has been the subject of a number of experimental work due to its high relevance in heterogeneous catalysis, particularly in relation with hydrogen fuel cells. Several studies have asserted the strong repulsion between these two species on the solid surface, especially in high pressures, wherein the formation of homogeneous islands of CO have been reported. On the other hand, theoretical work specifically addressing the H/CO coadsorption system on Pt is rather limited. To fully understand the physical mechanisms involved at the atomic scale, it would be beneficial for example to quantify the extent to which H and CO interaction on Pt is repulsive, knowing that H-CO interaction in the gas phase is actually partly attractive, and comment on possibilities for H and CO closely coexisting on Pt. It is in this light that we in this study describe the behavior of hydrogen near a Pt surface-adsorbed carbon monoxide molecule using a potential energy term constructed from ab initio calculations. The considerable asymmetry of the repulsion extent around CO suggests that while incoming hydrogen experiences strong obstacles to adsorption even before the Pt surface is reached, adsorbed H can remain stable even in relatively compact conditions. Inhibiting effects of CO greater than what is expected from simple adsorption site exclusion are discussed with regard to adsorption/desorption and mobility on platinum, as well as possibilities of COH and HCO formation on platinum. A quantum mechanical treatment of the H atom behavior similar to what we have used before[1] is also performed on the obtained potential term. Theoretical results are lastly discussed with available experimental data on the H-CO coadsorbate system on transition metal surfaces.

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**EN-TuP3 Electronic Energy Level Alignment in Dye Sensitized Oxide Substrates**, ***J.P. Theisen***, *S. Rangan, E. Bersch, R.A. Bartynski, J.D. Sorge, D.P. Birnie, Z. Duan, Y. Lu*, Rutgers University

In dye-sensitized solar cell applications, the HOMO-LUMO gap of dye molecules 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 used direct and inverse photoemission to measure the occupied and unoccupied electronic states of several dye-related molecules and determine their alignment with the band edges of single crystal and nanostructured $TiO_2$ and ZnO substrates. On well characterized rutile $TiO_2$(110) and wurtzite ZnO(11-20) single crystal surfaces, we have compared the position of the HOMO and LUMO levels of the N3 Ruthenium based-dye, of isonicotinic acid and catechol molecules. Isonicotinic acid, as a simpler form of the linker that binds the N3-dye on $TiO_2$, is found to have a very similar electronic structure as the N3-dye in the unoccupied states. This is consistent with the electronic transfer scheme where N3 excitation occurs from the HOMO localized on its Ruthenium center, to the LUMO delocalized on the dye linker to the surface. Catechol on $TiO_2$(110) however has no electronic states degenerated with the bottom of the conduction band edge. As a consequence the lower energy excitation process occurs via a HOMO to conduction band process. We have also measured the electronic structure of N3 adsorbed on more technologically relevant $TiO_2$ anatase nanoparticle and ZnO nanorod substrates.

**EN-TuP4 High Efficiency Down Converting Powder Phosphors for Solid Sate Lighting Applications**, ***S. Maslov***, *D. Bera, L. Qian, P.H. Holloway*, University of Florida

High performance blue and white organic light emitting diodes (OLED) offer improved efficiencies for solid state lighting. A down converting phosphor layer allows color tuning capabilities when coupled with a blue emitting OLED, and leads to improved efficacies approaching 80 lm/watt. The efficacy, CIE color coordinates, color rendering index, and angle resolved photoluminescence intensity were characterized versus film thickness and phosphor weight fraction. Due to scattering by phosphor particles, the initially forward focused light is converted to a Lambertian distribution of intensity. The method for applying powder thin films will be illustrated and discussed. The advantages and disadvantages of PMMA versus silicones for the dispersion matrix will be reported. Optimum phosphor layers were those with high quantum yield and maximum light out coupling.

**EN-TuP5 Ionic Conductivity of Scandia Doped Zirconia Thin Films by Oxygen-Plasma-Assisted Molecular Beam Epitaxy**, ***M.H. Engelhard***, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *S.V.N.T. Kuchibhatla, C.M. Wang, O. Marina, W. Jiang, V. Shutthanandan, P. Nachimuthu, R. Devanathan, L.V. Saraf, S. Thevuthasan*, Pacific Northwest National Laboratory

The development of electrolyte materials with high oxygen ion conductance at relatively low temperatures is essential to increase the efficiency and lifetime of electrochemical devices, such as solid oxide fuel cells (SOFC). Recently, there has been considerable interest in scandia stabilized zirconia (SSZ) since it shows high oxygen ionic conductance in comparison to commonly used ytrria stabilized zirconia (YSZ) in SOFCs. We have used oxygen plasma assisted molecular beam epitaxy (OPA-MBE) to synthesize high quality SSZ thin films on sapphire (0001) substrates and systematically investigated the conductivity as a function of temperature and Sc concentration. The epitaxial films have been characterized using various surface and bulk sensitive capabilities to determine their structure and composition. The ionic conductivity of SSZ depends not only on the dopant concentration, but also on the crystalline structure of the thin films. The optimum Sc dopant concentration for the highest conductivity was observed as 18 cation % in the temperature range of 500-900 °C. Conductivity appears to be significantly high in high quality cubic SSZ films in comparison to mixed phases of cubic and monoclinic. Molecular dynamics simulations of oxygen diffusion in cubic SZZ between 1125 and 2500 K show that the oxygen vacancy has no preference between Sc and Zr first neighbors, but the activation energy for O diffusion changes with Sc dopant concentration. Insights into the role of Sc dopant concentration on conductivity of SZZ obtained from experiments and simulations will be presented

**EN-TuP6 Chemical Mechanical Polishing Characteristics of CdS for CdS/CdTe Thin Film Solar Cell Applications**, ***H.-Y. Na***, *J.-S. Park, P.-J. Ko*, Chosun University, Korea, *N.-H. Kim*, Chonnam National University, Korea, *J.-T. Yang*, Gwangju College of Korea Polytechnic V, *W.-S. Lee*, Chosun University, Korea

CdS is widely used for the window layer material for the various thin film solar cells including CdS/CdTe, $CdS/Cu_2S$, and $CdS/CuInSe_2$ due to its excellent permeability with band gap of 2.42 eV while CdTe is one of the most promising photovoltaic materials with a direct band gap of about 1.45 eV, high optical absorption coefficients, the low cost, high efficiency and stable performance. The surface morphology of window layer materials was well known to affect the performances including the gain in photocurrent by increase of light scattering.[1] Therefore the surface morphology of CdS thin film as an window layer must be enhanced by the improved processes. Sputtering method was employed for preparation of CdS thin film, but it showed the rough surface morphology. Chemical mechanical polishing (CMP) processing was firstly proposed for improving the surface morphology of CdS thin film on behalf of the plasma treatment reported in some researches. Removal rate was estimated by the obtained results through the application to Hernandez power law as a generalization version of Preston's equation for a better description of removal rate. Surface roughness and within-wafer non-uniformity (WIWNU%) of the sputtered CdS thin film was also examined with a change of CMP process parameters including table speed and down force. The optimized process condition was selected considering to both the surface roughness and the hillock-free surface with the good uniformity.

[1] M. Phyton et al., J. Non-Cryst. Solids 2008.

**EN-TuP7 High Quality TCO Deposition using New DC Power Supplies**, ***D. Ochs***, HUETTINGER Elektronik GmbH + Co KG, Germany, *P. Ozimek*, HUETTINGER Electronic Sp z o. o., Poland

The main application of magnetron sputter processes for thin film solar cell production is the deposition of transparent conductive oxides (TCO). The most significant example for this TCO material class is ZnO:Al (AZO) which is of great importance as a transparent conductive layer for photovoltaic applications. Since this material has an especially high arcing rate, pulsed DC power processes have been used for deposition in the past. A new DC power supply family has been developed with the goal of replacing these pulsed DC processes with economic standard DC processes. The most important feature of this power supply is an extremely fast and advanced arc management with the capability to run stable processes with high arcing rates. The arc management has three different detection criteria: a voltage, a current and a combined voltage/current criteria. After detecting an arc, a positive voltage is applied to the cable between the power supply and cathode. This so-called Cable Length Compensation compensates the stored energy of the cable and reduces the energy supplied into the arc after power shut off. In this way residual arc energies of less than 0.5 mJ/kW, are achievable. Stable processes over a long time with arcing rates of up to 20,000 arcs/s become possible. The fast arc management with adaptable parameters results in superior film quality, and homogeneity of the deposited film. The new economic DC power supplies replace pulsed DC power without any disadvantages.

**EN-TuP9 Characterization of the Photovoltaic Heterostructure CdS:F/CdSTe***, ***F. de Moure-Flores***, *M. Meléndez-Lira, J.G. Quiñones-Galván, E. Mota-Pineda, S. Cerón-Gutiérrez*, CINVESTAV-IPN, México, *A. Hernández-Hernández*, Escuela Superior de Fisica Matemáticas-IPN, México, *M. González-Alcudia, M. Zapata-Torres*, CICATA-IPN Unidad Altamira, México, *C. Davet-Lazos, M.delaL. Olvera*, CINVESTAV-IPN, México

We present results of the characterization of the structural, electronic and electrical properties of the photovoltaic heterostructure: ITO / CdS:F / CdSTe. The ITO film was deposited by the technique of rf sputtering. The CdS layer was deposited employing chemical bath deposition adding fluorine to increase n-type doping. The top CdSTe layer was deposited by the modified laser ablation technique.[1] The motivation to deposit a CdSTe layer, instead just CdTe, is to limit the S interdiffusion at the CdS/CdTe interface in order to improve the characteristics of the interfacial electric field.[2] We report the characteristic I vs. V, the spectral response, as well as the efficiency of the photovoltaic heterostructure. These results are correlated with those obtained from the chemical, structural and electronic characterization obtained through EDX and X-ray diffraction and UV-Vis and Raman spectroscopies.

[*] This work is partially supported by CONACyT-Mexico

[1] M. González-Alcudia, A. Márquez-Herrera, M. Zapata-Torres, M. Meléndez-Lira and O. Calzadilla-Amaya, Adv. in Tech. of Mat. And Mat. Proc. J. 9, 81 (2007).

[2] M.A. Santana-Aranda, M. Meléndez-Lira, Applied Surface Science, 175-176 (2000) 538-542.

**EN-TuP10 Photoconduction Properties of Titanium Dioxide Films Prepared by Reactive Magnetron Sputtering**, ***H.A. Shukur***, Kogakuin Univeristy, Japan, *H. Nagai, I. Takano, M. Sato*, Kogakuin University, Japan

Since $TiO_2$ has been used as one of lower cost materials and is harmless to the environment, it is expected to use as a material of a clean energy system in future. Furthermore its photocatalysis have antifouling and antibacterial properties. At the same time, the electric property shows n-type semiconductor characteristics and is classified as a high dielectric material. However, details of electric property for $TiO_2$ have not been researched on the relations between the oxygen deficit state and light. Generally the resistance of $TiO_2$ is decreases by the excitation of electrons due to the light irradiation. We anticipate that these properties are applied to a photo sensor of electronic parts. In this study the electrical property of $TiO_2$ thin film was investigated under irradiation with the ultraviolet or visible light. The formation conditions was changed the substrate temperature 100 and 200°C. Furthermore $O_2$ flow rate was changed from 0.1 to 1.7 sccm for each substrate temperature. I-V property of films on a slide glass was measured by using an unresisted current meter under fluorescence light (FL), a black light (BL) or a sterilizing light (SL). The measurement size of the film was 200nm in thickness, 10 mm in length and 8 mm in width. The resistivity of films depends on $O_2$ flow rate. On the other hand the films resistivities in both temperature conditions hadn't a large different property until 1.3 sccm, but the films formed under substrate temperature 200°C showed a large resistvity. The microstructure of these films investigated by X-ray diffraction showed clearly that the both of $O_2$ flow rate and substrate temperature affected films in crystalline structure. In case of high substrate temperature and large $O_2$ flow rate, the crystalline structure of films changed to an anatase type and films resistivity was raised. The measurement of photoconduction current under each light irradiation showed two important results. Firstly the $TiO_2$ thin films obtained a large effect of photoconduction current under BL irradiation in all formation conditions. The second point was that the photoconduction current reduced with increase of the film resitivity and the maximum photoconduction current was obtained at the film of 0.5 sccm with both of a substrate temperature.

[1] Akira Fujishima, Kazuhito Hashimoto and Toshiya Watanabe, "$TiO_2$ Photocatalysis Fundamental and Applications".

**EN-TuP11 Effects of Pulse Sputtering Condition on Al: ZnO's Uniformities of TCO Properties for Solar Cell Application**, ***W.K. Yang***, *J.E. Jee, J.H. Joo*, Kunsan National University, Korea

Bipolar pulsed magnetron sputtering is used to deposit Al doped ZnO on a glass substrate for a TCO (transparent conducting oxide) in a solar cell structure. A 5”x25” AZO target was sputtered by 50 – 250 kHz bipolar pulsed dc power supply to deposit 400x400mm area by swinging back and forth. Sheet resistance, surface morphology and optical transmittance were measured at 16 slide glasses (1”x3”) to evaluate uniformity. In the thickness of 800nm, the average value of sheet resistance was 37Ω/□ and uniformity was 21.4% in 400×400mm area. The thickness of AZO thin film was 800nm and the resistivity was 2.9×10-3 Ω•cm. Generally, magnetron sputtering plasma is thought to be well confined above a target's race track. As substrate carrier is swinging, plasma is observed to be severely disrupted to go around to the back side at 5cm of target-substrate distance. To fully address these phenomena, we must use self consistent plasma model incorporating pulsed dc not just a simple dc cathode. As a first approach, we analyzed gas flow using a 3D fluid model as a substrate carrier is moving around a target and a gas distribution pipe. In here, we found that the gas flow distribution affected the plasma. Also we thought that this plasma might affect the deposited thin film. So, we expected that the uniform gas flow distribution could improve the plasma uniformity and the characteristics of AZO thin film.

**EN-TuP12 Germanium Nanowires: Applications in Photovoltaics and Electronics**, *L.A. Klein*, ***D.D.T. Mastrogiovanni***, *A. Du Pasquier, E. Garfunkel*, Rutgers University

Single crystal germanium nanowires are grown via vapor-liquid-solid methods in a hot-wall chemical vapor deposition reactor. We present the results of nanowire growth and discuss potential applications of nanowires grown on a variety of substrates. The relatively low growth temperature required for germanium nanowire formation combined with the enhanced semiconducting properties such as higher carrier mobility of germanium over silicon makes these wires an attractive building block in the rapidly expanding field of nanotechnology. In addition to our investigations into how growth conditions and substrates can affect the shape and orientation of the nanowires, we have investigated various chemical passivation methods, including chlorination, H-termination, and thiol and alkene passivation. Passivation becomes of utmost importance for germanium devices as germanium does not possess a stable native oxide as does silicon. These chemistries are also used to facilitate further surface functionalization and ohmic formation, and to improve device electrical performance. Most recently, the germanium nanowires were also used to enhance the properties of organic photovoltaic devices through the creation of a bulk heterojunction solar cell with poly(3-hexylthiophene) (P3HT). This hybrid-inorganic/organic device exhibits a significant increase in exciton dissociation and photocurrent when compared to pure P3HT. The photoelectrical properties of this device are characterized by measuring absorbance and photoluminescence spectra, current-voltage curves, and AM 1.5 filtered external quantum efficiency. In addition to the aforementioned techniques, other studies utilizing x-ray diffraction, Rutherford backscattering spectroscopy, and inductively coupled plasma mass spectroscopy enable us to observe how variations in nanowire concentration can affect the relative crystallinity and crystallite orientation of P3HT. We conclude with a discussion of our plans to improve the performance of these devices through surface passivation and the controlled introduction of phosphine impurities.

## Graphene Topical Conference
## Room: Hall D - Session GR-TuP

## Graphene Poster Session

**GR-TuP1 Growth Mechanism of Carbon Nanowalls Synthesized by Irradiation of Independently Controlled Ar Ions and $CF_X$/H Radicals**, ***S. Kondo***, *O. Stepanovic*, Nagoya University, Japan, *K. Yamakawa, S. Den*, Katagiri Engineering Co., Ltd., Japan, *M. Hiramatsu*, Meijo University, Japan, *M. Hori*, Nagoya University, Japan

Carbon nanostructures such as carbon nanotubes, fullerenes, etc. are investigated intensively in the world. Among a nanocarbon family, we are focusing on carbon nanowalls (CNWs). The CNWs can be described as two-dimensional carbon nanostructures with edges comprising stacks of plane graphene sheets standing almost vertically on the substrate. The CNWs have several unique characteristics, e.g. high aspect ratio and large surface area. Hence, the CNWs attract great attentions for nanoscale electronic devices, storage materials for hydrogen gas, and fuel cells. Previously, we have fabricated CNWs using parallel-plate capacitively coupled plasma with hydrogen (H) radical injection. Considering the practical applications of CNWs, further investigations are required to clarify the growth mechanism for control of their morphologies and properties. In this study, two radical sources, inductively coupled plasmas (ICPs) using 13.56 MHz, and an ion source, a ICP using 13.56 MHz, were used in order to understand which radicals or ions contributed to the CNWs formation. The heated Si substrate was exposed to fluorocarbon ($CF_X$) and H radicals as well as Ar ions, of which densities were controlled in each source independently. The correlation between the characteristics of irradiated species, such as Ar ion energy and H radical density, and the CNWs morphologies was investigated employing a spectroscopic ellipsometry for in-situ observation on the substrate surface. It was found that CNWs were not formed with Ar ions of energies below 100 eV with $CF_X$ and H radical injection. On the other hand, CNWs were successfully formed by Ar ions of energies between 100-200 eV, which were confirmed by SEM and Raman spectroscopy. The deposition rate of CNWs was proportional to the acceleration voltage of the Ar ions. As a result, not only fluorocarbon and hydrogen radicals but also high energy ions accelerated at energies of more than 100 eV were required for the nucleation of CNWs because higher energy ions created dangling bonds on the edge of CNWs, which will be a key for their growth. Furthermore, it was found out that the best value of hydrogen gas flow rate for the highest deposition rate and the better morphology of CNWs existed. The growth of high quality of CNWs with a high growth rate is determined by the balance of the ratio of H radicals to $CF_X$ radicals. These results will be crucial to elucidate the mechanism of CNWs.

**GR-TuP2 Enhanced Field Emission from Carbon Nanosheets by Thin Film Coatings**, *M. Bagge-Hansen, R.A. Outlaw, M.Y. Zhu*, ***D.M. Manos***, The College of William and Mary

Carbon nanosheets (CNS) are a promising two-dimensional carbon allotrope for high current field emission cathodes and are grown by radio frequency (RF) plasma-enhanced chemical vapor deposition from a $C_2H_2/H_2$ gas blend at substrate temperatures of ~ 600 °C. The resulting film consists of vertically oriented, honeycomb $sp^2$ carbon arrays terminating in single graphene sheets that serve as field emission cathodes. Conditioned films have previously been shown to provide high emission current density (~ 2 $mA/mm^2$), and stable lifetime (less than 5% variation over >200 h). The Fowler-Nordheim equation predicts that the field emission current density is a strong function of the local effective work function, e.g., a reduction of 1 eV in work function results in an increase in emission current of up to two orders of magnitude. Since the work function of graphite, carbon nanotubes, and amorphous carbon is relatively high, 4 - 5 eV, selective thin film coatings can substantially lower the effective work function at active emission sites. $Mo_2C$ and NbC films of ~1 nm have been grown on CNS by e-beam physical vapor deposition (PVD) in very high vacuum and subsequently characterized by Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) in UHV. Comparison of the as-grown CNS to coated CNS show large increases in current density; for example, a 2 nm coating of $Cr_2O_3$ /CNS gave an enhanced emission of a factor of 135. The emission shows a strong film thickness sensitivity that may be a consequence of band bending in the surface potential barrier. Coatings of $ThO_2$, $Cr_2O_3$ and $NbO_x$ on CNS have also been similarly grown and demonstrate similar improvements in current density.

**GR-TuP3 Thermal Desorption Study of Graphene Oxide**, ***D.A. Field***, *C.A. Ventrice*, Texas State University, *I. Jung, D. Yang, A. Velamakanni, R.D. Piner, R.S. Ruoff*, University of Texas

Graphene oxide is an electrical insulator that shows potential for use in nanoscale electronic devices. An understanding of the thermal stability of graphene oxide sheets is important since the electrical, chemical, and mechanical properties of graphene oxide will change as it is reduced at elevated temperatures. In this study, graphene oxide films were grown by deposition of an aqueous solution of graphene oxide onto oxygen plasma cleaned silicon nitride on silicon substrates. The thermal stability of these films was studied by temperature programmed desorption under ultra-high vacuum conditions. The primary decomposition components of the films are CO and $CO_2$. Analysis of the post-anneal chemical composition of the films was performed with x-ray photoelectron spectroscopy. Peaks associated with the C-C bond the C-OH, C=O, and C-O-OH functional groups are monitored at anneal temperatures up to 900 °C.

**GR-TuP4 Photoemission-Assisteded Plasma Chemical Vapor Deposition Synthesis of Nano-Grain Graphene on Mica and Silicon**, ***T. Takami***, Tohoku University and CREST JST, Japan, *E. Ikenaga*, Japan Synchrotron Radiation Research Institute and CREST JST, *M. Nihei*, Fujitsu Limited and CREST JST, Japan, *Y. Takakuwa*, Tohoku University and CREST JST, Japan

Multilayer graphene with nano-scale grain size has been formed on mica and silicon (100) surface with a plasma chemical vapor deposition method at the temperatures lower than 700 C from the mixture gas of methane and argon. The plasma was assisted with an irradiation of ultraviolet light to the sample, induced photoelectric effect. The grown nanographene has been confirmed by transmission electron microscopy and core-level X-ray photoemission spectroscopy with synchrotron radiation. The lattice images with transmission electron microscope and the diffraction patterns indicated that nanographene was formed on the substrates. The peak position of C1S band and pai-pai* plasmon loss band on the X-ray photoemission spectra also revealed the growth of graphene.

**GR-TuP5 Adsorption Kinetics of Alcohols on Single Wall Carbon Nanotubes**, *J. Goering, M. Komarneni*, ***U. Burghaus***, North Dakota State University

Carbon nanotubes can be used as supports for applications such as direct liquid fuel cell catalysts. The adsorption kinetics of alkanes (butane, pentane, hexane, trimethylpentane) and alcohols (methanol, ethanol, propanol, 2-propanol, butanol, pentanol, and hexanol) on single wall carbon nanotubes (HiPco-CNTs) supported on silica has been studied by thermal desorption spectroscopy (TDS). Multi-mass TDS indicate molecular adsorption/desorption with low coverage binding energies increasing linearly with the size of the alcohols. The coverage dependence of the heat of adsorption has been determined by a Redhead analysis. The heat of sublimation, determined by a leading edge analysis, increases linearly with the size of the alcohols whereas the zero order pre-exponential factor is approx. independent of the molecular size. Coadsorption TDS of alcohol-alkane mixtures indicate adsorption of these molecules inside of the CNTs. Adsorption probabilities of alkanes measured by molecular beam scattering increase while opening the CNT tube ends by annealing fresh samples. First results on CoMoCAT CNTs are presented in order to address a possible structure activity relationship.

**GR-TuP6 Fabrication, Structural Characterization, and Surface Modification of Carbon Nanoballs**, ***T. Ishizaki***, National Institute of Advanced Industrial Science and Technology, Japan, *N. Saito, O. Takai*, Nagoya University, Japan

Carbon related materials, eg, C60, CNT, diamond, and DLC, have attracted much attention and can be widely used in practical engineering fields. Synthesis of the carbon materials by chemical vapor deposition (CVD) have been considered as one of synthesis methods toward mass production. Carbon nanoballs (CNBs) can be also synthesized by the techniques that are normally used to produce carbon nanotube (CNT). CNBs have been expected to apply polymer composites and biological systems. In the case of application to the polymer composites, it is necessary to tailor the chemical property of the CNBs surface in order to covalently bind the polymer to the CNBs. In order to fabricate the CNBs-polymer composite, it is crucial to establish the surface modification method of the CNBs. In this study, we aimed to fabricate the CNBs by thermal CVD and to chemically introduce carboxylic acid groups to the CNBs surface. Fe-sputtered silicon wafer was used as a substrate. A target of Fe (99.99%) was used as received. A quartz tube in a ringed furnace was used as thermal CVD reactor. The substrate was placed on the center of the quartz tube. Reaction temperatures were changed from 750 to 990°C. The source gases were $H_2$ (100 sccm) and $CH_2$=$CH_2$ (25,75, 100, and 175 sccm). The samples obtained were characterized by FE-SEM, TEM, and Raman spectroscopy. The introduction of carboxyl groups to CNBs' surface were carried out by chemical wet process and vacuum ultra-violet (VUV) irradiation. The CNBs were successfully fabricated at the temperature of 850 and 990 °C. Raman spectra showed that the CNBs had two peaks at around 1350 and 1590 $cm^{-1}$, which correspond to D and G bands, respectively. The carboxyl groups were introduced to the CNBs surface by chemical wet process. The COOH-terminated CNBs were uniformly dispersed in water, ethanol, and acetone.

**GR-TuP7 Exposure of Epitaxial Graphene on SiC(0001) to Atomic Hydrogen**, ***N.P. Guisinger***, National Institute of Standards and Technology, *G.M. Rutter*, Georgia Institute of Technology, *J.N. Crain*, National Institute of Standards and Technology, *P.N. First*, Georgia Institute of Technology, *J.A. Stroscio*, National Institute of Standards and Technology

Graphene films on SiC exhibit coherent transport properties that suggest the potential for novel carbon-based nanoelectronics applications. Recent studies suggest that the role of the interface between single layer graphene and silicon-terminated SiC can strongly influence the electronic properties of the graphene overlayer. In this study, we have exposed the graphitized SiC to atomic hydrogen in an effort to passivate dangling bonds at the interface. We have used scanning tunneling microscopy to investigate the interface surface structure following exposure to atomic hydrogen for a range of sample temperatures. Initial results indicate that regions of clean SiC were successfully passivated with atomic hydrogen below 400 °C, while the underlying interface of the graphitized regions appear to be unchanged for all temperatures studied. The threshold temperature for passivating clean SiC suggest that the passivated dangling bonds are primarily from Si atoms that are present within the SiC surface reconstruction. Although the hydrogen does not appear to penetrate below the graphene layer, initial results suggest that it does adsorb to the graphene. *This work was supported in part by NSF grant ECS-0404084.

**GR-TuP8 Synthesis, Characterization and Luminescent Properties of ZnO-$SiO_2$:PbS**, ***O.M. Ntwaeaborwa***, *H.C. Swart, M.S. Dhlamini, J.J. Terblans, R.E. Kroon*, University of the Free State, Republic of South Africa, *P.H. Holloway*, University of Florida

PbS and ZnO nanoparticles prepared separately by a sol gel process were incorporated in $SiO_2$ by an ex situ method, resulting in a green emitting ZnO-$SiO_2$:PbS powder phosphor. Particle morphology, structure and chemical composition of the ZnO nanoparticles, PbS nanoparticles and ZnO-$SiO_2$:PbS composite were analysed with transmission electron microscopy, x-ray diffraction and x-ray photoelectron spectroscopy respectively. With or without ZnO nanoparticles, green photoluminescence with a peak at 540 nm was observed from $SiO_2$:PbS when excited with a 325 nm HeCd laser in air at room temperature. This peak was different from defect-related emission from ZnO nanoparticles observed at 570 nm. Again, it was different from the band edge emission from pure PbS nanoparticles observed at 1200 nm. The green photoluminesence at 540 nm was enhanced probably by energy transfer from incorporated ZnO nanoparticles. The origin of green photoluminescence from ZnO-$SiO_2$:PbS is discussed.

## MEMS and NEMS
## Room: Hall D - Session MN-TuP

## MEMS and NEMS Poster Session

**MN-TuP1 Effects of Gate Fabrication Processes on Electrical Characteristics in Suspended Gate FET**, ***T. Kumada***, *H. Kasai, M. Edo, Y. Ichikawa*, Fuji Electric Advanced Technology Co., Japan

Suspended gate FET`s (SG-FET) are expected to have a number of applications such as switching devices and acceleration sensors. A key process in these devices is how to fabricate the suspended gate. We have studied influence of the gate materials, the gate structure and sacrifice layer etching on the electrical characteristics of the SG-FET. The SG-FET we have developed has a conventional planar type MOS FET except for the gate placed apart from the silicon oxide gate insulator; the gate has a bridge structure with supports put outside the gate insulator. The gap between the gate and the gate insulator was designed to be 0.5 - 1.0µm. In these devices, the stress of the gate materials deforms the gate and changes the gap from the designed value; it affects the electrical characteristics of the SG-FET. Thus we have studied the gate materials and the gate structure to reduce deformation of the gate. Another important key in the SG-FET is the fabrication process of the suspended gate. To make its bridge structure, we deposit a sacrifice layer on the gate insulator first, and then deposit the gate material on it. After patterning it to form the gate, we remove the sacrifice layer by etching. This etching process affects the electrical characteristics of the SG-FET because of contamination and damage of the surface of the gate insulator. We applied polyimide to the sacrifice layer, and studied the influence of the etching method and the etching condition on the characteristics. In this presentation, we will discuss the relationship between the fabrication process and the materials of the suspended gate and the electrical characteristics in detail.

**MN-TuP2 Q-Factors of Suspended Al and Al-CNT Thin-Film Micromechanical Resonators as Function of Tensile Stress**, ***Y.J. Yi***, *J.H. Bak, Y.D. Kim, B.Y. Lee, S. Hong, Y.D. Park*, Seoul National University, Republic of Korea

We report on the Quality (Q) factor of micromechanical resonators, realized from suspended Al and Al-CNT nanolaminate thin-films,[1] as function of tensile stress. The doubly-clamped beam micromechanical resonators with varying dimensions are realized on GaAs substrate, which is selectively removed. Suspension of microresonators is preceded by UHV sputter deposition of Al and carbon nanotube (CNT) network assembly and patterning by standard e-beam and photolithography techniques. The frequency response of micromechanical resonators are characterized by a laser vibrometer-like set-up while the microresonators are actuated electrostatically. With significant difference in coefficients of thermal expansion, the suspended metallic thin-films have significant intrinsic internal stress as evident from fits to resonant frequency as function of beam dimensions measurements. The internal stress is further varied by post-fabrication thermal treatments as well as by chip-bending method.[2] Increase in Q-factors ultimately improves the force sensitivity of micromechanical resonator devices (i.e., mass sensing applications). Comparing the dependence of Q-factor to tensile stress of Al and Al-CNT thin-film microresonators allows for another avenue to study the mechanical enhancements due to CNT networks in the Al-CNT lamina.

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**MN-TuP3 Test Instrument for the Tensile Fracture Strength of Micro-Nano Materials**, ***A. Kasahara***, *H. Suzuki, M. Goto, H. Araki, Y. Pihosh, M. Tosa*, NRIM, Japan

Recent nano-technology researches have created various advanced micro-nano materials. In particular, there have been many reports on nano-meter-scale tubes and wires such as carbon nanotubes and silicon wires. We have prepared long crystal silicon wires with a diameter of several tens of nano meters at a temperature lower than 523k by using the low-pressure low-temperature CVD method. To use these as materials for application to micro-nano electromechanical system, we need to fully understand their electric, chemical and mechanical properties. As for the electric properties, current-voltage characteristics have been measured with the multi probe system using STM measurement units, although but there is almost few technique established for the measurement of mechanical properties. We have been therefore developing a strength measurement equipment for micro-nano materials to determine the mechanical properties of micro-nano wires in a vacuum for SEM observation. We will report this result on the development of test instrument to measure the tensile strength that can be observed with a desk-top simple SEM.

**MN-TuP4 Functionalization of Micro Mechanical Cantilever Sensors with $TiO_2$ and $\gamma$-$Fe_2O_3$ Nanocrystals**, ***C. Ingrosso***, *M. Striccoli*, CNR-IPCF Sez. Bari c/o Dip. di Chimica, Italy, *E. Sardella*, IMIP-Bari, Italy, *A. Voigt, G. Gruetzner*, Micro Resist Technology GmbH, Germany, *A. Agostiano*, CNR-IPCF Sez. Bari c/o Dip. di Chimica, Italy, *S. Keller, G. Blagoi, A. Boisen*, Technical University of Denmark, *M.L. Curri*, CNR-IPCF Sez. Bari c/o Dip. di Chimica, Italy

The oustanding flexibility of the surface chemistry of colloidal nanometer-sized particles[1] allows their reliable manipulation as building blocks and opens the access to the development of original supramolecular approaches, devoted to the mesoscale organization of nanoparticles in hierarchical structures. In this work, 3D arrays of organic-capped colloidal NCs were covalently immobilized on the surface of micro mechanical cantilever sensors made of a negative tone epoxy photoresist matrix. Mechanical cantilever sensors surface functionalized with a sensing active layer are very active in the detection of target molecules.[2] Q-sized colloidal NCs were immobilized at the surface of the miniaturized responsive components by means of the surface reactive residual epoxy at crosslinked photoresist matrix, which provide good accessibility to external interacting molecules, with an high immobilization capacity. The transferring of Q-sized colloidal NC properties to mechanically responsive miniaturized components represents an intriguing challenge, which disclose a great potential for extending the field of application of the ultrasensitive microfabricated mechanical cantilever sensors by exploiting novel transduction processes in molecule detection. Here, a simple solution-based method was adopted to modify the epoxy photoresist made cantilever surface with oleic acid (OLEA)-capped anatase $TiO_2$ nanorod (NR) and nearly spherical maghemite $\gamma$-$Fe_2O_3$ NC building blocks. The morphological evolution of the native epoxy surface upon the attachment of NCs was monitored by Atomic Force Microscopy (AFM), while the effective covalent anchoring of the nanoparticles was demonstrated by means of X-Ray Photoelectron Spectroscopy (XPS). The photo/catalytic, magnetic and optical functionalities of NCs[3] transferred to the high dense NC layout open the access to the development of novel MEMS/BIO-MEMS devices based on new bio/molecular recognition processes for bio/sensing or environmental purposes. Acknowledgements: The work was partially supported by the 7th FP EU project NOVOPOLY (STRP 013619)

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

### Poster Session

**NS-TuP1 Kinetic Control of Self-catalyzed Indium Phosphide Nanostructures**, ***R.L. Woo***, *L. Gao, S. Kodambaka*, University of California, Los Angeles, *N. Goel, M.K. Hudait*, Intel Corporation, *K.L. Wang, R.F. Hicks*, University of California, Los Angeles

Nanowire research has gained tremendous momentum due to its potential applications in nano-electronics, photonics, solar cells, and thermoelectrics. Precise control of size, morphology, density, and uniformity is essential for realizing these commercial opportunities. Most indium phosphide nanowire research is prepared by vapor-liquid-solid (VLS) growth using gold catalysts. However, gold incorporation into the InP is unavoidable and can adversely affect optoelectronic properties. As an alternative, we have investigated the self-catalyzed growth of InP using liquid indium droplets in a metalorganic vapor-phase epitaxy (MOVPE) process. In this study, three distinct shapes were obtained depending on the growth conditions: nano-wires, cones, and pillars. The shape of nanostructures is determined by the relative rates of indium phosphide deposition via vapor-liquid-solid and vapor-phase epitaxial growth processes. At the meeting, we will discuss more details on the underlying mechanisms of the crystal growth process and the relationship between the deposition mechanism and the resultant shape of the nanostructure.

**NS-TuP2 Polymer Transfer Printing for Chemical Patterns and its Application on Colloidal Assembly**, ***Y.H. Kim***, Furukawa Electric Co. Ltd., Japan, *B.S. Kim, P.T. Hammond*, Massachusetts Institute of Technology

A new approach to directly organize colloidal particles into patterned arrays using templates coated with a layer-by-layer assembled polyelectrolyte multilayer was introduced. In this approach, a template using a UV-curable photo polymer was coated with polyelectrolyte multilayers, followed by a contact printing of an oppositely charged polyelectrolyte monolayer. The resultant topological template with both positive and negative charges provided a finely defined chemical nano-pattern to guide selective deposition of colloidal particles onto the patterned surface upon Coulombic attraction. For example, when negatively charged dilute colloidal suspensions were placed on the template, the particles were selectively adsorbed within positively charged grooves or holes. Additionally, we have demonstrated development of uniform PEG copolymer chemical patterns via polymer transfer printing and their applications on direct assembly of two different sets of particles to different surface regions. This effective method provides a flexible and versatile route to the development of composite colloidal structures which will present interesting technological applications in photonics, electronics and sensors.

**NS-TuP3 Low-energy Electron Beam Calcination to Obtain Well-ordered Mesopores in Titanium dioxide Film**, ***A. Hozumi***, *H. Taoda*, AIST, Japan

Mesoporous materials fabricated using organic surfactant molecules or block copolymers as structural directing agents has attracted much attention not only catalysts and adsorbents, but also insulating layers, chemical and gas sensors, and optical and electrical devices. In order to fabricate microdevices based on such well-ordered mesoporous materials, the control of morphologies and geometries in nano ~ micrometer scale is one of the key technologies for practical uses. In this study, we report on a facile and rapid template removal method at low temperature to obtain mesoporous titania film without cracking. Our approach demonstrated here, named “low-energy electron beam (LEEB) calcination,” is a novel calcination technique based on the decomposition and oxidation of organic fractions such as surfactants or block copolymers by LEEB irradiation under vacuum. Organic templates can rapidly be eliminated from precursor mesocomposite film within 30 min without distorting periodic mesostructure, resulting in the successful conversion to crack-free ordered mesoporous titania film. Our best rate by LEEB calcination is ~14 times faster than the result obtained by photocalcination using 172 nm vacuum UV light.

**NS-TuP4 Structural and Morphological Evolution of Gallium Nitride Nanorods Grown by Chemical Beam Epitaxy**, ***S.-Y. Kuo***, Chang Gung University, Taiwan, *F.-I. Lai*, Yuan-Ze University, Taiwan, *W.-C. Chen*, *C.-N. Hsiao*, National Applied Research Laboratories, Taiwan

The morphological and structural evolution is presented for GaN grown by chemical beam epitaxy on (0001) Al2O3 substrates. Their structural and optical properties are investigated by x-ray diffraction, scanning and transmission electron microscopy, and temperature-dependent photoluminescence measurements. While increasing the growth temperature and the flow rate of radio-frequency nitrogen radical, the three-dimensional growth mode will be enhanced to form the one-dimensional nanostructures. The high density of well-aligned nanorods with a diameter of 30–50 nm formed uniformly over the entire sapphire substrate. The x-ray diffraction patterns and transmission electron microscopic images indicate that the self-assembled GaN nanorods are a pure single crystal and preferentially oriented in the c-axis direction. In addition, the enhanced A1(LO) intensity of micro-Raman spectrum confirms the formation of strain-free GaN nanorods in consistent with XRD and HRTEM results. Particularly, the “S-shape” behavior observed in the temperature-dependent photoluminescence might be ascribed to the fluctuation in crystallographic defects and composition. Neither catalyst nor template is required in our epitaxial system make this technique feasible to develop nanodevices based on strain-free III-nitride nanorods.

**NS-TuP7 Synthesis and Field Emission Properties of W18O49 Nanorods**, *K. Yong*, ***S. Jeon***, POSTECH, Korea

In recent years, the assembly of 1-D nanostructures in the fabrication of transition metal oxides has received increasing attention due to their interesting potential applications. Among these metal oxide nanomaterials, the fabrication of tungsten oxide nanostructures have been intensively studied due to their promising physical and chemical properties. In current study, we report for the first time the synthesis of tungsten oxide nanorods from tungsten-compound material using a simple annealing of the W2N/Si substrate. W2N film was deposited on Si(100) substrate by chemical vapor deposition at 450 °C and then heating of the film at 600 ~ 700 °C produces a high density of tungsten oxide nanorods. The morphology, structure, composition and chemical binding states of the prepared nanorods were characterized by SEM, XRD, XPS, EDX and TEM measurements. XRD and TEM analysis showed that the grown nanorods were single-crystalline W18O49. According to XPS analysis, the W18O49 nanorods contained ~62% of W6+, ~28% of W5+, and ~10% of W4+. Field emission measurements showed a low turn-on field of 9.5 V/μm for the W18O49 nanorods, indicating that they can be used as potential field emitters.

**NS-TuP9 Fabrication of Three-Dimensionally Periodic Macroporous $TiO_2$ Thin Film for Photovoltaic Application**, *S.B. Yoon*, *Y.H. Kim*, *K. Kim*, *B.-C. Woo*, Korea Research Institute of Standards and Science, *S.J. Chung*, Korea Research Institute of Biosience and Biotechnology, ***W.S. Yun***, Korea Research Institute of Standards and Science

Three-dimensionally (3D) periodic macroporous $TiO_2$ thin film was fabricated by using polystyrene sulfonate (PSS) nanoparticle as an organic template and titanium alkoxide as a $TiO_2$ precursor on fluorine-doped tin oxide (FTO) glass. Close-packed colloidal crystalline thin film composed of PSS nanoparticles was prepared by using 2D deposition technique. The $TiO_2$ precursor was immersed into the void space between PSS nanoparticles and subsequently in-situ hydrolysis and condensation were performed. The nanocomposite of PSS nanoparticles and amorphous $TiO_2$ was calcined to remove the organic materials and to crystallize the amorphous $TiO_2$ to anatase type at 450℃ under air flowing. Resultant anatase $TiO_2$ thin film was exhibited the 3D periodic macroporous framework with connecting windows. Photovoltaic cells composed of the Ru-dye coated 3D periodic macroporous anatase $TiO_2$ thin film were fabricated and their energy conversion efficiency was also investigated.

**NS-TuP10 Vapour Phase Deposition of Aromatic Self-Assembled Monolayers**, ***L. Kankate***, *H. Muzik*, *A. Turchanin*, *A. Gölzhäuser*, University of Bielefeld, Germany

Self-assembled monolayers (SAMs) with aromatic moieties recently caused a particular interest due to their applications in molecular electronics,[1] nanolithography[2,3] and biotechnology.[4] For high quality SAM-based devices and nanostructures, a reproducible fabrication of high quality SAMs is necessary. The traditional “wet” preparation of SAMs may suffer from solvent, ambient and substrate contaminations resulting in poor quality and degradation of the molecular assemblies. On the contrary, the preparation of SAMs in UHV can provide a high degree of control over the experimental parameters. We have studied the formation of 1,1’-biphenyl-4-thiol (BPT) and 4’-nitro-1,1’-biphenyl-4-thiol (NBPT) SAMs on gold surfaces by vapour deposition in UHV. The vapour deposited monolayers were characterized by mass spectrometry, X-ray photoelectron spectroscopy (XPS). and scanning tunnelling microscopy (STM). Based on this data, the deposition parameters were optimized. A comparison of vapor deposited SAMs with monolayers prepared from solution is presented.

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**NS-TuP11 Characteristics of La-substituted Bismuth Titanate Ferroelectric Nanofibers by Electrospinning**, ***K.T. Kim***, University at Buffalo, the State University of New York, *C.I. Kim*, Chung-Ang University, Korea, *Y.K. Yoon*, University at Buffalo, the State University of New York

The bismuth layer-structured ferroelectrics have been known as high dielectric materials with attractive properties such as environmentally friendly lead-free composition and fatigue free characteristic. Specially, the La-substituted Bismuth Titanate ($Bi_{3.25}La_{0.75}$ $Ti_3$ $O_{12}$ :BLT) has received the intensive attention for their excellent ferroelectric, crystalline properties as a promising dielectric for capacitors and memory devices.[1] Recently, there has been an intense research effort on one dimensional nano materials such as nanotube and nanofiber due to their unique structure and properties, such as high aspect ratio, large specific surface area and chemical/mechanical stabilities.[2] In this study, BLT nanofiber synthesis has been demonstrated using electrospinning and subsequent sintering. A composite solution consisting of a metal-organic decomposition solution of BLT and a binder of poly(vinylpyrrolidone) (PVP) has been electrospun in an electric field of $3 \times 10^5$ V/m to form nanofiber with a diameter of 120 nm. The BLT/PVP composite nanofiber has been calcined in air for 1 h at 500, 600, 700, 750, and 800 $^{o}$C, respectively. The characteristics by X-ray diffraction, FT-IR, SEM and HR-TEM of the BLT/PVP composite nanofibers are reported.

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**NS-TuP12 Nanostructured Glassy Carbon Supported GC/Pt Electrodes for Model Studies of Fuel Cell Relevant Electrocatalytic Reactions**, ***Y.E. Seidel***, *A. Schneider*, *L. Colmenares*, *Z. Jusys*, *R.J. Behm*, Ulm University, Germany, *B. Wickmann*, *B. Kasemo*, Chalmers University of Technology, Sweden

In this contribution, we discuss the potential of nanostructured planar electrodes for model studies of electrocatalytic reactions relevant for Polymer Electrolyte Fuel Cell (PEFCs). The model electrodes consist of catalytically active Pt nanostructures of well-defined size and separation, which are supported on planar glassy carbon substrates.[1,2] They are fabricated employing colloidal lithography (CL)[1] or Hole-mask Colloidal Lithography (HCL),[2] or by micellar techniques, via deposition of metal loaded micelles and the subsequent removal of the polymer stabilizer.[3] Both techniques allow us to independently vary size and separation of the catalytically active nanostructures/particles. The resulting particle sizes are ca. 3-15 nm (micellar techniques) and 70-150 nm (CL, HCL), respectively. These nanostructured model electrodes allow direct and quantitative access to an important aspect of electrocatalytic reactions which so far has been largely neglected, to the influence of mesoscopic transport effects on the characteristics of electrocatalytic reactions. Using the reduction of $O_2$ and the oxidation of formaldehyde as examples it will be shown that mass transport effects not only modify the overall rate, but have significant effect also on the product distribution, e.g., on $H_2O_2$ formation. Possible contributions of the reactant transport to the overall reaction process will be discussed in a molecular picture.

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### NS-TuP13 Dimer Ordering of M-TtertBuPc on Graphite, ***T. Takami***, *C. Carrizales, K.W. Hipps*, Washington State University

The growth and ordering of metal complexes of 2,9,16,23-tetra-tert-butyl-phthalocyanines (TtertBuPc) on graphite surface have been studied by scanning tunneling microscopy. A well-ordered molecular layer having the molecular plane lying parallel to the graphite substrate was obtained at the solution - graphite interface at room temperature. For Cu-TtertBuPc, dimer ordering similar to that reported previously on the Si(111)-r3Xr3-Ag surface[1] was partly observed. We will also discuss the effects of changing the center metal and/or the phthalocyanine to naphthalocyanine, and imaging and orbital mediated tunneling spectroscopy in ultrahigh vacuum (UHV).

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### NS-TuP14 Optical Performance of EUV Lithography Mask with Silver Doped Zinc Oxide Absorber, ***H.Y. Kang***, *M.K. Kim, C.K. Hwangbo*, Inha University, Republic of Korea

The lithography performance of extreme ultraviolet lithography (EUVL) mask depends on the correct choice of absorber materials because it is directly related to imaging contrast, shadowing effect, focus shift effect, and thermal effect.[1] The optical constant of the absorber materials in the EUV region should have higher extinction coefficient for higher attenuation. Also, the absorber material should exhibit good conductivity, which can alleviate the charging effect during electron-beam patterning. In the past, a wide range of materials (Ti, TiN, Al–Cu, TaSi, Ta, TaN, Cr, etc) has been evaluated as possible conductive absorbing materials for EUVL mask.[2,3] The total thickness of the absorber stack by using the materials used to be greater than 80 nm because the available absorbing materials are limited and an anti-reflection coating is necessary to maximize pattern inspection efficiency at deep ultraviolet wavelength. It is reported that the large thickness of the absorber stack may cause a geometric shadow effect in an exposure step and as a result, the printed patterns are shifted and biased.[4] In this study, we propose a new absorber stack with a silver doped zinc oxide absorber layer. The optical constants of ZnO layers with various concentration of Ag at 13.5 nm are calculated. It is found that the optical constants of ZnO layers with high concentration of Ag show lower refractive index and higher extinction coefficient at 13.5 nm than those of TaN layer. Thus ZnO layers doped with Ag enables EUVL masks to be designed to have very small height difference between high reflecting and absorbing stacks, suggesting that the geometric shadow effect can be significantly reduced.

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### NS-TuP15 Actinide Powder Characterization for Nuclear Forensics, ***W.S. Duncan***, *A.D. Neuman, C.C. Davis, T.A. Nothwang*, Los Alamos National Laboratory

Half of the Department of Energy's nuclear forensics scientists are expected to retire within the next 15 years but there continue to be around 10 confirmed cases of nuclear material trafficking each year.[1,2] The Interfacial Science team of LANL's Materials Science & Technology division is addressing this need for new nuclear forensics expertise by helping to create a database of actinide powder characteristics. This poster addresses physical characterization on a nanoscale level via microscopy and other methods in order to obtain microstructural and elemental composition as well as crystal structure of known powders.

[1] Mayer, K., et al., CSI: Karlsruhe. Actinide Research Quarterly, 2007. 4th quarter: p. 1-9.

[2] McKenna, Phil. NewScientist.com news service. 16 February 2008. http://www.newscientist.com/article.ns?id=dn13336.

### NS-TuP16 Template-Free Synthesis and Characterization of Copper Oxide Nanostructures, *K.-R. Lo, **C.-C. Chang***, National Taiwan University

As a relatively non-toxic p-type semiconductor and a classical example of excitonic solid, cuprous oxide may play an important role in the electronics industry as the dimensions of electronic devices continue to shrink. For example, devices made of nanometer-scale cuprous oxide are expected to be small and fast because the electrical signal can resonantly tunnel through the nanoscale cuprous oxide layers. In addition, cuprous oxide structures fabricated in the nanoscale may exhibit better antifouling and algicide effects, increase its overall water splitting capability for solar energy applications, and enhance its photocatalytic activity for degradation of organic pollutants under visible light. Nanoscale cuprous oxide structures were prepared in this study via a template-free synthetic approach in the ethylene glycol solution using different copper compounds as the precursor. SEM images and Auger spectra revealed that, instead of forming spherical particles, micro- to nano-sized aggregates of well-defined geometric shapes were obtained. These aggregates were made of nanocrystalline particles, as revealed in high-resolution TEM and diffraction studies, which self-assembled into organized solids. XPS spectra suggested that the crystallization and the self-assembling may take place via cuprophilic attraction. The shape and the dimensionality of the assemblage obtained can be controlled by adjusting reaction temperature and/or by using different surfactants. Chemical conversion of cuprous oxide to cupric oxide impaired the cuprophilic interaction, leading to dismantling of the assemblage at extended reaction time. The chemical process and the mechanism involved in the assembling and dismantling of the polycrystalline assemblage will be discussed.

### NS-TuP17 Preferred Diameter Growth of Single-Walled Carbon Nanotube by using Sapphire Substrates, *K.-Y. Shin*, National Tsing Hua University, Taiwan, ***J.-S. Kao***, National Applied Research Laboratories, Taiwan, *K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotube (SWCNT) has been considered as an alternative material for nano-devices, such as carbon nanotube field-effect-transistor or nano-sensor. It has been found that the characteristics of the SWCNT-based device are affected by the band gap of the tube, which depends on its diameter and chirality. Preferred diameter growth of single-walled carbon nanotube (SWCNT) by using single crystal sapphire (0001) and sapphire (110-2) substrates is reported. The carbon nanotubes were grown by mono-layered iron catalyst from sapphire substrate and a mixture of methane and hydrogen at 900°C by chemical vapor deposition. Atomic force microscopy revealed that the particle size distribution of catalyst was varied with different orientation sapphire substrate. The micro-Raman spectra exhibited that the radial-breathing mode signals of SWCNTs grown by Fe (1nm) catalyst were shifted with different orientation sapphire substrates. A growth model based on minimum strain theory (i.e. O-lattice theory) and surface tension theory is proposed.

### NS-TuP19 Fabrication of Porous Si Using Anodic Aluminum Oxide, ***N.Y. Kwon***, *K.H. Kim, J.M. Kwon, I.S. Chung*, Sungkyunkwan University, Korea

Porous Si templates with various pore patterns were obtained by etching underlying Si using an anodic aluminum oxide (AAO) mask. Si3N4 imprint stamps with a nano size matrix pillar (height : 50 nm) pattern were indented into Al film grown on Si wafer using an oil press method with the force of 5kN·cm-2. After indenting on Al thin film (thickness : 200 nm), we found that the periodic array with 30 nm depth was formed on Al thin film using scanning probe microscopy. The indented Al film was then anodized using two different anodizing conditions, namely, 0.3M oxalic acid of 4°C at 50V and 0.3M sulfuric acid of 10°C at 25V, and these conditions were suitable to define the matrix pore pattern. As pore's size and interval were decided by anodizing conditions, pre-patterning must set to anodizing condition to get regular pattern. We can control the size of pore and the interval of pore by modifying the aforementioned anodizing conditions. Thus, we can achieve a well organized Si porous template by transferring AAO pattern using ICP etcher with 30 W of rf power, 30 mTorr total pressure, 30 SCCM of CF4, and 4 SCCM of O2.

### NS-TuP20 Fabrication and Characterization of One-Dimensional Semiconducting Nanowire That Use AAO, ***K.H. Kim***, *N.Y. Kwon, J.K. Hong, I.S. Chung*, Sungkyunkwan University, Korea

In this study, we attempted to fabricate and characterize one dimensional semiconducting nanowire(CdSe, Polypyrrole). It is well known that CdSe is n-type material, whereas polypyrrole is p-type material. The template used in the nanowire growth was AAO(Anodic Aluminum Oxide) template. After forming AAO template on Al foil, the oxidized underlying barrier layer was removed using a cathodic polarization method based on KCL(0.5mol, -5V, 4℃) solution. Then, nanowires with 50nm diameter and 300nm height were grown using the electroplating method. Finally, the nanowires were characterized using SPM(Seiko Instruments, SPA 300HV) by proving the conductive cantilever. I-V characteristics as a function of the temperature gives an activation energy which is useful to understand the conduction mechanism of semiconducting nanowires.

**NS-TuP22 Nanopatterning by Near-Field Photodeprotection of 2-Nitrophenylpropyloxycarbonyl-Protected Aminosiloxane Monolayers on Glass**, ***S. Alang Ahmad,*** University of Sheffield, UK, *L.-S. Wong,* University of Manchester, UK, *E. Haq, J. Hobbs, G. Leggett,* University of Sheffield, UK, *J. Micklefield*, University of Manchester, UK

Nanometre scale control of chemical reactivity is key for many applications of nanotechnology in biology, electronics, materials science, etc. Currently there are few methods for the selective initiation of chemical transformations with nanometre precision. Here we report a novel approach to nanopatterning in which a scanning near-field optical microscope coupled to a near-UV laser is used to selectively deprotect 2-nitrophenylpropyloxycarbonyl (NPPOC) protected aminosiloxane monolayers on glass. Initially, UV deprotection was studied for unpatterned samples using X-ray photoelectron spectroscopy and contact angle measurements. The resulting amine-terminated surfaces were activated with glutaraldehyde and then derivatized using a fluorinated adsorbate and aldehyde polymer nanoparticles. Contact angle and XPS measurements indicate extensive surface functionalisation. Next, micrometre-scale patterns were fabricated using mask-based exposure to light from a He-Cd (325 nm) or Ar-ion (364 nm) laser, and characterised by friction force microscopy. Nanoparticle patterns were formed by covalent attachment methods. Nanometre scale patterns were fabricated using near-field exposure, and characterised by FFM. The nanopatterns were derivatised with functionalised molecules, showing that high spatial resolution (ca 100 nm) was readily achievable, and also that extensive functionalisation of the patterns could also be accomplished.

## Plasma Science and Technology
## Room: Hall D - Session PS-TuP

## Plasma Science Poster Session

**PS-TuP2 Invesitgation of Growth Mechanism of Diamond-like Carbon Film**, ***M. Shinohara,*** *Y. Matsuda, H. Fujiyama,* Nagasaki University, Japan, *T. Nakatani*, Toyo a-tec Co. LTD., Japan

There has been much interest in diamond-like carbon (DLC) films because they have a lot of useful properties: mechanical hardness, chemical inertness, and changeable electrical properties. Further, DLC films were deposited at low temperatures by using plasma process. The films have been used as coating materials for mechanical apparatus. On the other hand, DLC films should be used as electrical and electronic device materials, if the deposition of DLC films has to be controlled in atomic level. Therefore, it is important to understand the growth mechanism of the DLC films. Only a few papers proposed growth mechanism: the deposition rates of DLC films were decreased with the increases of the substrate temperatures; this was because the hydrogen radical generated in plasma was etched the carbon films. However there are a lot of problems left in this model. Thereby, we investigate the growth mechanism in PECVD process by using infrared spectroscopy and deposition/etching rates. We found the decrease of the deposition rates was not due to the hydrogen radical etching, but to the decreases of the adsorption coefficient of hydrocarbon radicals generated in plasma. This was because the etching rates were not increased by the increases of the substrate temperatures. We also found that the types of hydrocarbon species in the DLC films were changed by the substrate temperatures less than 300 degree C during the deposition; in this temperature region the hydrogen was not thermally desorbed from the films. It is due to the activation of the hydrogen abstraction effects by the increases of the substrate temperatures.

**PS-TuP3 Impact of Combinatorial Plasma Process on the Development of Organic Low-K Dielectric Film Etching**, ***C.S. Moon,*** *K. Takeda,* Nagoya University, Japan, *M. Sekine, M. Hori,* Nagoya University and Japan Society of Technology Agency, *Y. Setsuhara,* Osaka University and Japan Society of Technology Agency, *M. Shiratani*, Kyushu University and Japan Society of Technology Agency

Plasma etching technology is one of technologies, which have been in charge of semiconductor device industry. As it is scaled down to several tens of nanometers, the sophisticated plasma parameter control has been indispensable to achieve the process requirements. However, up to now, it was an obvious fact that a lot of trials and errors have been carried out in the development of plasma etching process by external parameters such as input power or working pressure, since there has never been the any scientific guiding principle based on plasma science. We hereby propose the development of process map called Plasma Nano Science. However, as the enormous database is necessary to establish the process map, it is difficult by conventional unit process capable of obtaining one result by one trial. At this moment, we have newly developed the combinatorial plasma process apparatus for etching of organic low-k dielectric film, which enables to acquire many results by just one experiment. Desktop-typed combinatorial plasma apparatus was realized by capacitively coupled plasma source consisted of top electrode (13.56MHz) with the diameter of 10 mm and bottom electrode (2MHz) with that of 40 mm. Process gases of hydrogen and nitrogen were used for etching organic low-k dielectric film. Optical emission intensity of combinatorial plasma was investigated by ICCD camera and we could confirm the formation of intentional non-uniform plasma with gradient on the bottom electrode. The spatial distributions of H and N radical densities were measured by compact vacuum ultraviolet absorption spectroscopy (VUVAS) system designed and developed by our group[1] and the etching characteristics of combinatorial plasma process were interpreted by radical density. As a result, impact of combinatorial plasma process on the development of organic low-k dielectric film etching in terms of internal parameters was confirmed for the first time. The combinatorial plasma process will open a new avenue for the establishment of plasma nano science.

[1] S. Takashima, M. Hori, T. Goto, A. Kono, M. Ito and K. Yoneda, Appl. Phys. Lett. 75, 3929 (1999).

**PS-TuP4 Surface Fluorination of Ultra High Molecular Weight Polyethylene using Electron Beam Generated Plasmas**, ***S.G. Walton,*** *E.H. Lock,* US Naval Research Laboratory, *A.A. Bujanda, D.D. Pappas*, US Army Research Laboratory

The intrinsic bulk properties of polymers make them ideally suited for light-weight, conformal protective outerware or devices. Their surfaces properties, on the other hand, require modification to realize their full potential and plasma treatment is one of the most powerful techniques to tailor the functionality of polymer surfaces. In this study, we use pulsed, electron beam generated plasmas to modify the surface of ultra high molecular weight polyethylene (UHMWPE) films. One advantage of these plasmas is the ability to regulate the ion flux and energy at the polymer surface. Under typical operation, the kinetic energies of the incident ions are at or below the energies of the polymer bonds, thus limiting damage caused by ion bombardment. The plasma-polymer interaction produces fluorine-containing groups on the surface, leaving the polymer bulk properties unaffected. Preliminary results indicate that the plasma-treated surfaces exhibit increased hydrophobicity, X-ray photoelectron spectroscopy (XPS) shows the presence of chemically bonded fluorine groups on the surface, and AFM indicates minimal changes in surface morphology. The results from these studies are used to understand the fluorination of ultra high modulus polyethylene fibers under similar plasma conditions. This work was supported by the Office of Naval Research. EHL is an NRC/NRL Postdoctoral Research Associate.

**PS-TuP5 Measurement of the Isoelectric Point of Plasma Modified Surfaces and Plasma Polymerized Thin Films**, *S. Pease,* ***E.R. Fisher***, Colorado State University

Plasma polymerization and plasma modification are often used to tailor the surface properties of materials. One important, but often overlooked property of materials is the isoelectric point, which is a critical measure of the acid/base properties of a variety of surfaces, most notably metal oxide surfaces. The isoelectric point for surfaces can be determined using contact angle methods as a function of the pH of the water solution used for the measurements. Here, we have treated a variety of metal oxide surfaces, including $SiO_2$, $SiO_xN_y$, and $ZrO_2$ with Ar plasmas to determine the effect of plasma treatment as well as aging on the isoelectric point of the surfaces. $SiO_2$ substrates exhibit a significant increase in isoelectric point upon treatment, from ~4.9 to ~6.0, depending on substrate location in the plasma. Upon aging, there is no change in the isoelectric point. In contrast, the $SiO_xN_y$ substrates exhibit little change in isolectric point upon treatment, and no subsequent changes are observed upon aging. XPS compositional data will also be presented to corroborate changes in surface composition upon treatment as well as upon aging of the substrates. Additional contact angle and XPS data will be presented on plasma-deposited metal oxides (e.g. $SiO_x$ and $SiO_xC_y$) and polymers (e.g. poly(allyl alcohol) and polyamides) for comparison.

**PS-TuP6 Plasma Processing with $CH_3OH$**, ***K.J. Trevino***, *E.R. Fisher*, Colorado State University

Traditional plasma processes including deposition, etching, and surface modification have been utilized in a variety of commercial applications. These applications can require highly toxic and expensive monomers; to avoid these issues, we have been exploring the use of $CH_3OH$ for a variety of both nontraditional and traditional applications. First, the non-traditional application for plasmas of contaminated water remediation, has been explored using $CH_3OH$ as a model compound for organic contaminants. It was chosen as a standard to compare larger organic molecules to in the future for detection and abatement with optical emission spectroscopy (OES). These studies were performed in a glass tubular reactor equipped with OES detection. Results for both $CH_3OH$ and methyl tert-butyl ether (MTBE) contaminated water demonstrated that not only is detection of organic molecule breakdown possible, but abatement can also be achieved. Our data demonstrate this for CH3OH and MTBE at detectable limits of 0.01 ppm. Second, data for OH radicals from our imaging of radicals interacting with surfaces (IRIS) technique will be presented for both $CH_3OH$ and $H_2O$ plasmas. These two simple systems allow us to understand the behavior of OH radicals from different precursors. Results from these studies will be compared to previous studies, especially with respect to how plasma parameters affect the underlying chemistry occurring in the plasma. Finally, preliminary results will be presented from studies designed to explore the use of $CH_3OH$ plasmas as an etchant. These studies were completed in a capacitively-coupled parallel plate reactor (PPR) and include OES, scanning electron microscopy (SEM), and profilometry measurements. Comparison to traditional halogenated systems will also be presented.

**PS-TuP7 Efficiency Improvement of Organic Solar Cells with Plasma Patterning and Surface Treatment*, H. Chae*, *C. Pang, K. Park, D. Jung, H. Kim*, Sungkyunkwan University, Republic of Korea**

Plastic organic solar cells are getting attention due to its possible advantages in flexibility and processing costs. In this presentation, brief review of issues of plastic solar cells will be discussed with possible solutions. Our approaches to improve efficiency of plastic solar cells with plasma processing of electrodes will be discussed in details. One of the approaches is to improve the efficiency of polymer solar cells by patterning indium tin oxide (ITO) electrode layer. Light absorbance was enhanced with ITO layer patterning for the improvement of power conversion efficiency of polymer solar cells. The line-and-space pattern of polystyrene layer is formed on the top of 100nm thick indium tin oxide layer by capillary force lithography process and the patterning. And surface roughening of the ITO layer were completed with O2 and Ar plasma etching with various step heights of 20nm to 60nm. We have shown that the patterning of the ITO can increase the efficiency of the plastic solar cells. Another approach to be discussed is plasma surface modification of the solar cell electrodes. Plasma processing of the ITO surface with fluorocarbon plasmas and oxygen plasma increased the efficiency of the plastic solar cells by removing organic contaminants in the ITO surface and by surface oxidation.

**PS-TuP8 Polymer Modification by Electron Beam Generated Plasma in Argon, Oxygen and Nitrogen Environments and Their Mixtures**, ***E.H. Lock****, S.G. Walton*, Naval Research Laboratory

The electron beam generated plasmas are efficient at generating high density plasmas over the volume of the beam, resulting in large fluxes of low-energy ions (< 5 eV) at surfaces located adjacent to the electron beam. Thus, the ion energy applied to the surface is comparable with the bond strengths found in most polymers, so it is sufficient to invoke chemical surface modification with limited morphology changes. In this study, polymer modifications resulting from electron beam plasma generation in argon, oxygen and nitrogen environments and their mixtures are investigated. The polymers of interest include polystyrene, polymethylmetacrylate and ultra-high molecular weight polyethylene. The effects of the plasma process parameters including treatment time and duty factor, as well as mixture composition on surface energy, chemistry and morphology are investigated.

**PS-TuP9 Synthesis of Polyethyleneglycol and Polystyrene-Like Films by Atmospheric and Low Pressure Plasmas**, *D. Merche*, ***B. Nisol***, Universite Libre de Bruxelles, Belgium, *C. Poleunis, P. Bertrand*, Universite Catholique de Louvain, Belgium, *F. Reniers*, Universite Libre de Bruxelles, Belgium

The deposition and characterization of polystyrene (PS)-like and polyethyleneglycol (PEG)-like on a variety of substrates was investigated using “plasma enhanced chemical vapour deposition” (PECVD) under atmospheric pressure. For both PS and PEG-like deposits, an atmospheric RF plasma torch (Atomflo® 250C SurfX) was used, which consists of two closely metallic electrodes that are perforated to allow the process gas (Ar) to flow through. The precursors (styrene vapour or tetraglyme droplets) were introduced into the plasma downstream to the electrodes (remote plasma). Thin films of polystyrene were also synthesized in a home-built dielectric barrier discharge (DBD), in remote and direct HF plasma. Precursor vapours (styrene) are carried out by Ar or He. PEG-like films are also obtained at low pressure, in a capacitively coupled RF discharge obtained in a cylindrical Pyrex system. PEG-like films are known for their non-fouling property, which is an important feature for many biomedical applications. XPS and SSIMS were useful in order to ensure that the precursor for PEG like films are not too strongly fragmented by plasma treatment, in which case the protein-repelling property of the samples would be compromised. XPS permits to determine the C/O of PEG-like. The non-fouling properties of those samples have been studied with Bovine Serum Albumin (BSA) adsorption. XPS was used to track the presence of proteins on the surface by using the N1s signal coming out from the protein. pp-PS films deposited on PTFE were characterized by XPS. Spectra show a significant change in C1s energy value (towards lower binding energies) in comparison with untreated PTFE. We can also observe an important amount of oxygen, indicating a strong oxygen functionnalization into the film. Consequently, the pp-PS are more hydrophilic (water contact angle) in comparison to conventional PS. The influences of the parameters and the plasma source on the FTIR spectra (IRRAS) of plasma polymers deposited on steel (pp-PS) and on gold surface (PEG-like) was investigated. FTIR on pp-PS shows a decrease of the aromaticity, and that the films are branched, cross-linked and contain hydroxyl groups. The morphology of pp-PS films were evaluated by optical microscopy.

**PS-TuP11 Dry Etching Properties of TiN for Metal/High-k Gate Stack by using $BCl_3$-based Inductively Coupled Plasma**, ***C.-I. Lee***, Ansan College of Technology, Korea, *D.-S. Um, D.-P. Kim, G.-H. Kim, J.-C. Woo, C.I. Kim*, Chung-Ang University, Korea

Transistor has been scaled down since they were introducing, continually. However, it is accompanied with several problems like direct tunneling through the gate dioxide layer and low conductivity characteristic of poly-Si gate in nano-region. To cover these faults, study of new materials is urgently needed. This can be achieved by using an insulator that has a high dielectric constant. Recently, high dielectric materials like $Al_2O_3$, ZrO2, and $HfO_2$2 are being studied for equivalent oxide thickness (EOT). However, poly-Si gate is not compatible with high-k materials for gate-insulator. Poly Si gate with high-k material has some problems such as gate depletion and dopant penetration problems. Therefore, new gate structure or materials that are compatible with high-k materials are also needed. TiN for metal/high-k gate stack is conductive enough to allow a good electrical connection and compatible with high-k materials. So, it is a good barrier-layer material for interconnection. According to this trend, the study on dry etching of TiN for metal/high-k gate stack is needed. In this study, the investigations of the TiN etching characteristics were carried out using the inductively coupled $BCl_3$-based plasma system and adding $O_2$, Ne, and $N_2$. Dry etching of the TiN was studied by varying the etching parameters including $BCl_3$/Ar gas mixing ratio, RF power, DC-bias voltage to substrate, substrate temperature and gas addition. The plasmas were characterized by optical emission spectroscopy analysis and quadrupole mass spectrometer measurements. The chemical reaction on the surface of the etched TiN was investigated with X-ray photoelectron spectroscopy. Scanning electron microscopy was used to investigate the etching profile.

**PS-TuP12 Dry Etching of CoFeB Films using $BCl_3$-based Inductively Coupled Plasma for MRAM Application**, ***D.-S. Um****, D.-P. Kim*, Chung-Ang University, Korea, *S.K. Lee, T.W. Jung*, Hynix Semiconductor Inc., Korea, *C.I. Kim*, Chung-Ang University, Korea

We have been in the personal computing age, but person and computer are harmonized uneasily with each other. Now, however, it is within the range of possibility. Recently many researchers are studying about ubiquitious that can provide users to access computers at anytime and everywhere. If we could make devices of smaller size, higher speed and lower power consumption, it can be realized. Magnetic RAM(MRAM) using tunnel junction is the device which can meet this requirement. Tunnel junction is consisted of two ferromagnetic layers separated by an insulator. One of the ferromagnetic layers is pinned-layer that fixed magnetization, whereas the other ferromagnetic layer is free-layer unfixed magnetization. Due to spin dependent electron tunneling one can thus have two distinct resistance states, associated with the magnetizations of the pinned and free layers parallel or anti-parallel. To improve device performance, one continuously aims to achieve higher tunnel magnetoresistance (TMR), better thermal stability and low ferromagnetic coupling between pinned and free layers. The use of amorphous CoFeB films in the free and pinned layers of optimized tunnel junctions enabled us to obtain a higher TMR coefficient, good transport properties upon annealing and lower coupling fields. Up to now, there are few papers on the plasma etching of CoFeB films using high density plasmas. However, those papers did not show the changes of component on the etched surface of CoFeB. In this study, CoFeB films were etched with using the inductively coupled plasma system and $BCl_3$-based gas chemistries. Etch rate and selectivity of the CoFeB was systemically studied by the process parameters including $BCl_3$/Ar gas mixing ratio, RF power, DC-bias power, substrate temperature. The changes of electron temperature, ion energy and radical volume densities were characterized by optical emission spectroscopy analysis, Langmuir prove and quadrupole mass spectrometer. The etch rate of CoFeB showed highly dependency on the DC bias voltage and pressure due to effective removal of etch byproducts from the exposed CoFeB surface in plasma by sputtering de-sorption. The changes of components on the surface of CoFeB were investigated with X-ray photoelectron spectroscopy. The variation of surface was also investigated with atomic force microscopy and scanning electron microscopy.

**PS-TuP13 Temperature Dependence on Dry Etching of $Al_2O_3$ Thin Films in $BCl_3/Cl_2/Ar$ Plasma, *X. Yang***, *D.-P. Kim, D.-S. Um, C.I. Kim*, Chung-Ang University, Korea

High-κ gate dielectrics and metal gate electrodes are required for enabling continued equivalent gate oxide thickness scaling, and hence high performance, and for controlling gate oxide leakage for both future silicon and emerging non-silicon nanoelectronic transistors. Significant progress has been achieved in terms of the screening and selection of high-κ insulators, understanding their material and electrical properties, and their integration into CMOS technology. During the etching process, the wafer surface temperature is an important parameter which influences the reaction probabilities of incident species, the vapor pressure of etch products, and the re-deposition of reaction products on feature surfaces. It mainly depends on the chuck temperature, the ion density and ion energy and the exothermicity of the etching reaction. In order to obtain the good etching environment, sudden changes of temperature in the plasma condition during the transition between processes steps should be well controlled .In addition, the true substrate temperature is difficult to monitor. For this reason, the experiment according to the substrate temperature change was progressed. In this study, we investigated that the effect of substrate temperature on the etch rates and selectivity of $Al_2O_3$ over Si and hard mask materials (such as $SiO_2$, and $Si_3N_4$) thin film in inductively coupled plasma in function of $(BCl_3/Ar)+ Cl_2$ gas mixture ratio, RF power, DC bias and chamber pressure base on the substrate temperature increases from 10 °C to 80 °C,. The chemical reactions on the etched surface were investigated with using x-ray photoelectron spectroscopy. The morphology changes of exposed surface in plasma were investigated with atomic force microscopy. The etch profile was evaluated with SEM as functions of parameters.

**PS-TuP14 Aspect Ratio Dependent Twisting and Mask Effects During Plasma Etching of $SiO_2$ in Fluorocarbon Gas Mixtures*, *M. Wang***, *M.J. Kushner*, Iowa State University

During plasma etching of via-like structures having high aspect ratios (HAR > 10), twisting is sporadically observed. This is where an otherwise straight feature will turn from the vertical. Twisting may occur in only a few percent of features among other features that have unaltered profiles. The effect is most frequent when feature size openings to the plasma are only tens of nm. Twisting in plasma etching of $SiO_2$ has been computationally investigated using the Hybrid Plasma Equipment Model to obtain the energy and angle distribution of ions and neutrals; and the Monte Carlo Feature Profile Model to predict profiles. The basic operating conditions are a capacitively coupled plasma sustained in $Ar/C_4F_8/O_2 = 80/15/5$ (1 kW, 10 MHz, 40 mTorr, 300 sccm). Parametric investigations were made while varying aspect ratio (10-40), height of the photoresist mask, power deposition and reaction probabilities (e.g., angular dependence of scattering). When including charging, features should be resolved with atomic-scale resolution to eliminate numerical effects. We found that as the feature size decreases, the flux entering the feature becomes more stochastic in nature. This randomness in the flux can then lead to variations in both the total etch rate on a feature-to-feature basis as well as on the profile. For example, preferential polymer buildup on one side of the feature may produce asymmetric etching. These effects are magnified when including charging as the stochastic nature of the flux produces errant local electric fields that deflect ion trajectories. The height and character of the mask material potentially has an important role in twisting. The photoresist height contributes to the effective aspect ratio; and its electron and ion scattering characteristics contribute to deliver of charge deeper into the feature.

*Work supported by the Semiconductor Research Corp., Micron Inc. and Tokyo Electron Ltd.

**PS-TuP15 The Analysis of $ZrO_2$ Thin Films Etching in $BCl_3/Cl_2$ Inductively Coupled Plasma, *H.-J. Kim***, *D.-P. Kim, G.H. Kim, J.-C. Woo, D.-S. Um*, Chung-Ang University, Korea, *C.-I. Lee*, Ansan College of Technology, Korea, *C.I. Kim*, Chung-Ang University, Korea

As feature size of CMOS device has been decreased 100 nm, the new material has required to substitute for $SiO_2$ as gate dielectric material. The silicon oxide for gate reached a physical limit owing to very high gate leakage current of 10 $A/cm^2$ for very thin gate $SiO_2$ of below 1nm. Therefore, high dielectric constant materials, such as $HfO_2$, $ZrO_2$, and Al2O3 have attracted a great attention. Among them, $ZrO_2$ is the most candidate because of its high dielectric constant of 20 ~ 25, wide bandgap of 5~7 eV, and thermal stability with Si. In order to obtain a small feature accurate pattern transfer, development of plasma etching process for $ZrO_2$ thin film is important problem to be solved. There are few papers on the etch of $ZrO_2$ thin films with using helical resonator plasma and electron cyclotron plasma in $Cl_2/BCl_3$. They reported that etch rate of $ZrO_2$ is limited by the low volatile etch by product such as $ZrCl_2$, but the etch rate can be accelerated by the addition $BCl_3$ which can be effectively remove oxygen from the surface of $ZrO_2$. However, there is no relationships between input parameters and plasma chemistry as well as surface reactions. In present work, the etching characteristics of $ZrO_2$ thin film was investigated with using inductively coupled $BCl_3/Cl_2$ plasma. $ZrO_2$ thin film was deposited on Si substrate by atomic layer deposition (ALD). The variation of etch rate and selectivity was monitored while additive gases was varied in $BCl_3/Cl_2$ plasma. Simultaneously, the etch behavior of $ZrO_2$ was investigated with variation of RF power, DC bias voltage, and pressure. To understand the influence of additive $O_2$, He or $N_2$ into $BCl_3/Cl_2$ on the electron temperature and the density of radicals, Langmuir probe (LP), optical emission spectroscopy (OES), quadrupole mass spectromter (QMS) was used during etching process.

**PS-TuP16 Effective Measurements of Plasma Process-Induced Damage Related to Dielectric Integrity Degradation on Gate Oxide using Practical Structure, *J. Lee***, *H. Lee, H. Kim*, Samsung Electronics, Korea, *I.S. Chung*, Sungkyunkwan University, Korea

Monitoring techniques are required to understand the root cause of the damage and how to optimize the process or equipment. Many techniques for plasma damage monitor were introduced.[1,2] But it was difficult for them to identify the plasma process-induced damage because of unrealistic and complicated structures. Therefore, the plasma process was optimized and verified with newly-designed test structure to monitor wafers. The presented structure based on an unconventional antenna structure is very simple but effective to measure the plasma charging damage, which correlates to real circuit performance, such as parametric shifts, hot carrier response, and dielectric integrity degradation[3]. It was composed of various antenna ratios, active areas, and patterned features for detecting electron shading effect, plasma non-uniformity and ion bombardment damage. Electrical tests including threshold voltage shift, hot carrier stress, and breakdown voltage have been performed to detect plasma damage.

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**PS-TuP17 Reaction Mechanisms and Profile Evolution for $HfO_2$ High-K Gate-stack Etching: Integrated Reactor and Feature Scale Modeling*, *J. Shoeb***, *M.J. Kushner*, Iowa State University

To minimize leakage currents resulting from the thinning of the insulator of the gate-stack of field effect transistors, high-k metal oxides, and $HfO_2$ in particular, are being implemented as a replacement for $SiO_2$. To speed the rate of processing, it is desirable to etch the gate stack (e.g., metal gate, anti-reflection layers, dielectric) in a single process while having selectivity to the underlying Si. Plasma etching using $Ar/BCl_3/Cl_2$ mixtures have been shown to effectively etch $HfO_2$ while having a good selectivity with respect to Si. In this talk, we discuss results from integrated reactor and feature scale modeling of gate stack etching in chlorine plasmas. The stack consists of an erodible photoresist mask, metal gate and $HfO_2$ with underlying Si (and possibly anti-reflection layers). Reactant fluxes were obtained from reactor scale modeling of inductively and capacitively coupled plasma tools using the Hybrid Plasma Equipment Model. Surface reaction mechanisms were developed using its Surface Kinetics Module. The mechanisms were implemented in the Monte Carlo Feature Profile Model with which etch profiles are predicted. We found that $BCl_x$ species produced by electron impact in the plasma react with $HfO_2$ which, under ion impact, form volatile etch products such as $B_xOCl_y$ and $HfCl_x$. Selectivity to Si is achieved by boron creating Si-B bonding as a precursor to the deposition of $BCl_x$ polymer, which slows the etch rate relative to $HfO_2$. The low ion energies required to achieve this selectivity then challenge one to obtain highly anisotropic profiles in the metal gate portion of the stack. Validation was performed with data from the literature. Results will be discussed from parametric studies of process variables (e.g., gas mixture, power, bias) on etch rate and profile.

*Work supported by the Semiconductor Research Corp.

**PS-TuP18 A Reduced Model for Etch Rate Prediction Based on Plasma Parameters, *M. Klick***, *L. Eichhorn, R. Rothe*, Plasmetrex GmbH, Germany

The virtual metrology is the prediction of plasma etch rates and critical dimensions is based on measurements of pre-process values and plasma parameters. This can be realized by a self-consistent model of plasma and process or non- self-consistent (empirical) model with plasma parameters measured in real-time and in situ. A self-consistent plasma model must describe the complete plasma process. Already the real-time solution for a self-consistent plasma model is impossible, in particular due to large amount of also chemical mechanisms. The effort can be reduced dramatically by usage of plasma parameters, describing the main physical and chemical mechanisms. The most important issue of development of a chemical / physical model is to identify the key parameters. Tool parameters reflect only the tool properties but not the real process. The most important process parameters, called key parameters, are plasma density and electron collision rate by SEERS (physics), RF-parameters by VI-probe, radical/polymer concentrations by OES (chemistry). Our reduced approach for reactive ion etching as described above assume a combination of a physical (sputter) effect, a pure chemical (surface) reaction, and a physical-chemical mechanism. Despite the pressure is usually kept constant, the real important parameter is the density of the gas (neutrals) which depends on the temperature additionally. The gas temperature is usually not available but replaced here by the electron collision rate which is proportional to the gas density and so reciprocally proportional to the gas temperature. The model was applied to oxide etch with F-chemistry, the unknown coefficients were determined and prediction error was shown to be less than 5%.

**PS-TuP19 Molecular Dynamics Simulation of Si Etching by Monoenergetic $Br^+$, $Br_2^+$, $H^+$, and $HBr^+$ Ions Generated in HBr Plasmas**, ***T. Nagaoka**, H. Ohta, K. Eriguchi, K. Ono*, Kyoto University, Japan

Dry processing technology with chemically reactive plasmas has been widely utilized for the fabrication of semiconductor devices. At present, HBr plasmas are standard for Si etching processes (e.g., gate etch and shallow trench isolation etch in the fabrication of SRAM). Here we first report molecular dynamics (MD) simulation of Si etching by HBr or $Br_2$ plasmas. The Simulation procedure is as follows. In the 3D simulation cell (cross section=$3.2^2$ $nm^2$, depth = about 5 nm), about 1,500 silicon atoms are initially located in the structure of diamond lattice. Atoms in the bottom layer are fixed and periodical boundaries are imposed in the horizontal direction. To this Si(100) substrate, 20-300 eV ions are impinged in the direction normal to the surface. In this study, we used an improved Stillinger-Weber interatomic model partially including multibody interaction. Parameter sets for Si/H/Br were newly determined based on ab-initio data. We focused on monochromatic beam etching by $Br^+$ ($Cl^+$), $Br_2^+$ ($Cl_2^+$), $H^+$, and $HBr^+$ ions without radicals. First, we confirmed the different etching characteristics between cases of Br and Cl. Yields by $Br^+$ and $Br_2^+$ were lower than those by $Cl^+$ and $Cl_2^+$ at the same ion energy. This tendency agrees with experimental results.[1] Additionally, yields by diatomic ions were higher than those by monatomic ions. The energy dependence of etch yield will be presented. Secondly, we estimated the halogen coverage. The Br coverage for $Br^+$ impact was lower than Cl coverage for $Cl^+$ impact. For the case of $Br^+$ with an ion energy of 50 eV, the depth of reaction layer and Br coverage were about 20 Å and $7.7\times10^{14}$ $cm^{-2}$, respectively. On the other hand, for $Cl^+$ impact, the depth of the reaction layer and Cl coverage were about 30 Å and $1.7\times10^{15}$ $cm^{-2}$, respectively. These coverages are in good agreement with experimental results of $6.0\times10^{14}$ $cm^{-2}$ and $1.0\times10^{15}$ $cm^{-2}$ using HBr and $Cl_2$ plasmas, respectively, where a dc bias voltage is -35V.[2] In this conference, the effect of $H^+$ on etching mechanisms will be also discussed.

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**PS-TuP20 A Novel Interatomic Potential Model for MD Simulation of Si Etching by $Cl^+$/$Br^+$ Containing Plasmas**, ***H. Ohta**, T. Nagaoka, K. Eriguchi, K. Ono*, Kyoto University, Japan

Plasma-surface interaction is an important research subject both academically and industrially. Particularly, the understanding of interaction between chemically reactive plasmas and semiconductors is inevitable for further improvement in the fabrication of semiconductor devices. At present, HBr plasmas are utilized for state-of-the-art fine Si etching processes. However, fundamental experimental data were not sufficient except for some plasma experiments.[1] In addition, potential models for Si/F and Si/Cl systems were only available for Si etching simulations. Here we present an novel interatomic potential models to realize classical molecular dynamics (MD) simulation of Si etching by HBr plasmas. Our simulation target is Si etching by HBr or $Cl_2$ plasmas. First, the scheme to construct potential function was renewed, where all parameters could be systematically determined based on ab-initio data obtained from quantum chemical calculation. As a potential form, we selected the well-known Stillinger-Weber (SW) model, where the total potential is expressed by the sum of two- and three-body functions. SW model could reproduce ab-initio data with high accuracy when systems include only two or three atoms. Secondly, a new discipline to construct potential model is also proposed. We clarified how the potential functions affect etching characteristics in MD simulations.[2] Until now, SW potential models for etching simulation were determined on the basis of potential energies calculated for small clusters while the energies for ion penetration and stay in interstitial sites have not been considered. However, the latter crucially affects the results of etching simulation, especially the morphology of the reaction layer. Then, the accurate estimation of potential energies for ion penetration in interstitial sites is essential for qualitative improvement of etching simulations. After careful examination, it was founded this energy was overestimated when the original SW model was used. Based on this fact, we proposed an improved SW model, where a new term is added to three-body potentials. In this conference, we present a detail derivation of the new model and the comparison between results by old and new SW models.

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**PS-TuP21 Numerical Simulations for a Radio-Frequency Micro-Atmospheric Pressure Plasma Jet and Coupling with Laser Diagnostics**, *J. Waskoenig, **K. Niemi**, T. Gans*, Queen's University Belfast, Northern Ireland

Atmospheric pressure plasmas in particular micro-discharge devices have tremendous application potential and are already used and targeted for a variety of technological and bio-medical applications. Micro-atmospheric pressure plasma jets (μ-APPJs) can provide high concentrations of radicals at a low gas temperature, particularly for modification of sensitive surfaces, such as in biomedicine or for surface coatings. Nevertheless the fundamentals of these non-equilibrium plasmas at ambient pressure are only rudimentarily understood. In general, the diagnostics of atmospheric pressure plasmas is extremely challenging, therefore numerical simulations offer a further insight into these discharges. The presented 1D-model is a numerical fluid-model along/across the discharge gap for a μ-APPJ. Dual frequency (2f) excitation of the μ-APPJ promises enhanced efficiency concerning the radical production and additional control for the plasma production. The discharge dynamics of the 2f excitation is investigated in various parameter ranges. Modelling and numerical simulations are however mainly restricted due to the lack of available data, particularly for surface processes which are crucial at these small dimensions because of the extraordinary high surface to volume ratios. Using experimentally measurable quantities as fixed input parameters of the model offers the opportunity to overcome this lack of available data. The μ-APPJ has been specially designed to provide an excellent optical diagnostic access to the discharge volume. Absolute atomic radical densities can be measured using two-photon absorption laser-induced fluorescence spectroscopy for use as a fixed input parameter in the model. Absolute measurements require detailed knowledge of collisonless de-excitation processes in particular under atmospheric pressure conditions. This can be obtained from the effective fluorescence decay rate (estimated lifetime of about 100 ps). The required temporal resolution can be achieved using a tuneable UV Fourier-limited picosecond laser system (1 $cm^{-1}$, 10 ps). Within the simulation the sticking coefficient for atomic oxygen loss at the electrode surfaces is varied until consistency with the locally measured atomic oxygen ground state density is reached.

**PS-TuP22 A Comprehensive 3D Fully Coupled Model of a Gas Discharge for the Simulation of Magnetron Sputtering Systems**, ***F.J. Jimenez**,* University of Alberta, Canada*, D. Field,* NuCryst Pharmaceuticals, Canada*, S. Ekpe, S.K. Dew*, University of Alberta, Canada

Sputter deposition is a well established technique underlying a wide range of technological applications. However, the system is complex, involving coupled interactions of plasma, target, transport and substrate. Several models have been developed to explain and to optimize the process conditions. Nevertheless, the majority of these models excluded or simplify some key parameters missing the benefits that may arise using a detailed model. We present a comprehensive 3D coupled model where each part of the process is isolated in modules. Transport of charged and neutral particles is solved using a hybrid algorithm where energetic particles are followed individually using a Direct Monte Carlo (DMC) approach and thermalized particle transport is described by a computational fluid dynamics model modified to account for the nonuniform magnetic field. The plasma model is solved self-consistently using an octree grid with local refinement in the region next to the cathode to resolve the thin sheath typical of magnetron sputter systems. The highly coupled system of partial differential equations is numerically solved using a modified Newton method. An iterative approach is used to surmount the coupling arising between the glow discharge and the rarefaction and heating of the background gas. For experimental verification, a planar magnetron with an Aluminum target has been used as the reference system. The discharge has been characterized using a custom Langmuir probe. Plasma densities are shown to increase with power and pressure as would be expected. Electron temperature on the other hand decreases with pressure and power for the process conditions studied (5-40 mTorr, 75-300 W). At high pressures and/or high powers, the rate of reduction in electron temperature decreases, suggesting the effect of process gas rarefaction. At these pressures and powers significant rarefaction has been observed indicating a trend between this effect and plasma parameters. This may suggest a more decisive role of the gas-plasma interaction when modeling magnetron sputtering systems in this pressure regime.

**PS-TuP23 Kinetic Simulations of Dielectric Facing Plasma and Sheath under Application of Microwave Energy**, ***D. Smithe***, Tech-X Corporation, *R. Bravenec*, Tokyo Electron America, Inc., *P. Stoltz, C. Roark*, Tech-X Corporation, *M. Funk, L. Chen*, Tokyo Electron America, Inc., *E. Kase*, Tech-X Corporation

Generation and heating of plasmas by microwaves to an overdense state $(\omega<\omega_{pe})$, where the waves should be cut off, is not completely understood. We study sheath formation and behavior at the interface between an insulating dielectric and an un-magnetized plasma, using electromagnetic particle-in-cell simulation techniques.[1] Various scenarios are of interest here, including both situations in which the plasma is under-dense and over-dense, or transitions from under-dense to over-dense. In the case of over-dense plasma, we look at situations involving incident electromagnetic radiation resulting in field components both parallel and perpendicular to the plasma interface, and are interested in the skin-depth penetration of the waves into the plasma. Of particular interest is the resonance of the EM waves at the location in the sheath where the wave frequency matches the plasma frequency and can serve as the major source of heating of over-dense plasmas[2] The simulations include the effects of ionization, and allow us to study the buildup of plasma density associated with ionization in the presence of the large fields of the RF-enhanced sheath. The ionization model is a Monte-Carlo type model, with energy dependant cross-section.[3] We are also studying the effects of secondary emission processes from the dielectric interface. For example, copious secondary emission is seen to reduce or even momentarily reverse the sign of the sheath. Our secondary emission model[4] was originally designed for metallic emission surfaces, but it being re-engineered to treat secondary emission from dielectric materials. It allows for energy and incident angle dependant yield, and produces a specific energy spectrum of outgoing particles. The overall goal of this work is to develop an analytical or tabular model of the sheath for use in fluid models of plasma.

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**PS-TuP24 Effects of Etching-Mask Geometry and Charging on Etching Profile Evolution**, ***H. Fukumoto***, *H. Ohta, K. Eriguchi, K. Ono*, Kyoto University, Japan

Two-dimensional etching profile evolution in two different geometries, an axisymmetric hole and an infinitely long trench, has been calculated to clear effects of etching-mask geometry and charging on etching profile evolution. In the simulation, $SiO_2$ etching by fluorocarbon plasmas is assumed because of widely employed processes for the fabrication of contact and via holes in the $SiO_2$ film. The model takes into account the transport of particles in microstructures, together with surface reactions therein through sputtering, ion-assisted etching, chemical etching, and deposition. The model includes ions and neutrals ($CF_x^+$, $CF_x$, F; x=1-3) coming from the plasma, under different conditions of particle temperature, density, and ion energy. The neutral particles from the plasma onto substrate surfaces are assumed to travel in microstructures with diffusive reflections on feature surfaces, while the ions accelerated through the sheath on the substrate travel with specular reflections on feature surfaces. The cell removal method is employed to represent the feature profile evolution, where the $SiO_2$ is represented by two-dimensional discrete cells. Numerical results indicate that the etching profiles of hole and trench have the similar tendency under varying input parameters such as plasma species densities, ion energy, and mask aspect ratio. However, the etching-mask geometry shows some differences in the two structures; the resulting profile is narrower and shallower in the hole than in the trench, where the incident neutral fluxes are more reduced in the hole. Moreover, the profile of the trench has lateral etches such as undercut and bowing on sidewalls. The velocity distribution of neutral particles contributes to the difference of the etching profile evolution in the two structures; in effect, the velocity distributions are the more isotropic in the trench, because less neutral particles interact with mask sidewalls in the trench. Thus, it follows that geometrical structures contribute significantly to the behavior of neutral particles therein, and characterize the resulting etched profiles. The etching-mask geometry and the $SiO_2$-etched feature also make the differences in charging potential at the feature bottom in the trench being lower than in the hole, because the trench feature surface obtains more electron flux owing to its geometrically smaller shadowing effect.

**PS-TuP25 Plasma Surface Texturing of Metals**, ***E. Park***, *K. Casey, M. Morud, K. Taylor*, Medtronic, Inc.

A novel plasma process for creating a nanometer and micron-scale textures on MP35N alloy surfaces using radio-frequency (RF) inert gas plasmas was investigated, with a focus on characterizing the relationship between process variables and the resulting microstructure. This unique plasma texturing technology provides several advantages over other coating-based texturing processes. Because it is a surface modification process, coating delamination and loose particulates, which would cause serious problems in biomedical applications, are not of concern. Possible applications of the textured surfaces include drug reservoirs, surfaces that promote tissue or bone in-growth, and any applications benefited by high surface areas. In the plasma texturing process, metal samples were placed directly on the substrate holder that was electrically connected to an RF electrode. Typical process parameters for Ar plasma texturing included 200W to 800W of power, pressures of 20 mTorr to 80 mTorr, and process times of 8 min to 10 min. A variety of surface textures with differently sized features have been formed varying from individual pillars to three dimensional, interconnected porous structures. The microstructures that evolve were believed to result from the loss of material from the metal sample, due to the combination of interactions of Ar ions with the sample and subsequent heating of the metal surfaces. The amount of material removed from MP35N alloy samples during texturing ranged from 4 to 10 % of the initial mass of the sample depending on the degree of texturing. Process variables, including RF energy and pressure, as well as properties of the material to be textured (thermal and electrical transport properties and sample geometry) were all found to affect the degree of texturing and type of microstructure formed. To create surfaces with more complex textures, the plasma textured surface has been modified by subsequent surface treatments and depositions. This secondary process can form additional microstructures on the already textured surface or modify surface chemistry and properties.

## Surface Science
## Room: Hall D - Session SS-TuP

## Surface Science Poster Session

**SS-TuP1 A Study of a Hydrogen Atom on Pd-Ag Alloy Surfaces Via First Principles Calculation**, ***N. Ozawa***, *T. Roman, H. Nakanishi, H. Kasai*, Osaka University, Japan

Technology for extracting hydrogen gas with high purity from natural gases is necessary for the establishment of a hydrogen fuel system. At present, since materials used for permeable films such as Pd are rare and expensive, a fundamental understanding about reaction processes of hydrogen on metal surfaces is necessary for developing an alternative material replacing with them. On the time, we have studied the elementary reaction processes of a hydrogen atom on Pd surfaces and its subsurface[1-4] using first principles calculations. In particular, we have given focus on quantum mechanical behaviors of the hydrogen atom motion, which appear due to the small mass of hydrogen. In this study, we investigate the quantum states of the hydrogen atom on the PdAg alloy surface and in its subsurface by calculating the wave functions and the eigen energies for the hydrogen atom motion within the framework of the variation method on an adiabatic potential energy surface (PES) obtained from the first principles calculations.[5,6] From these researches, we discuss the behavior of the hydrogen atom such as adsorption and diffusion. We find that the adsorption energy of the hydrogen atom on the surface and activation energy for diffusion into the subsurface area are smaller than on pure Pd surfaces. In this conference, we also discuss the hydrogen atom behavior on the other kinds of Pd-based alloy surfaces.

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**SS-TuP2 Size-Dependent Surface Chemistry of Alumina Nanoparticles**, ***P.L. Brazee***, Smith College, *D.M. Dukes, L. Schadler*, RPI, *K.T. Queeney*, Smith College

The particle size of a number of different oxide materials has been found to influence cell adhesion and growth; specifically, nanophase (rather than conventional micron-sized) particles enhance these processes. The increased adsorption of proteins to nanophase particles has been implicated in this size-dependent phenomenon. The current study focuses on the surface chemistry of alumina particles as a function of average particle size, specifically to determine whether or not there are size-dependent differences in surface chemical species that may affect protein (and other biomolecule) adsorption. Alumina nanoparticles of varying phase and diameter were spin-coated onto silicon substrates and their uniformity characterized via SEM and XPS. The distribution of surface hydroxyl (OH) species was analyzed via transmission infrared (IR) spectroscopy. The OH stretches observed for all alumina samples are signficantly redshifted (~200 $cm^{-1}$) from the frequencies observed for dried alumina powders (e.g. using diffuse reflectance IR). While a common cause of such redshifting in ν(OH) peaks is hydrogen bonding with surface water, the spin-coated samples do not exhibit the concomitant peak broadening associated with this kind of hydrogen bonding. We propose that the unique ν(OH) signatures of spin-coated alumina particles arise from discrete hydrogen bonding interactions between alumina hydroxyls and surface silanols on the underlying silicon substrate. Differences in the OH-stretching peaks for different phases (e.g. γ vs. α) of alumina provide evidence that these features do, in fact, arise from the alumina particles themselves. We do in fact see a size dependence in the distribution of surface hydroxyl species, with distinct populations of different OH species arising from conventional vs. nanophase alumina of all phases studied. These differences are likely to arise from different relative populations of edge vs. facet sites as a function of particle size.

### SS-TuP3 Surface Electronic Structure of Epitaxial $La_2NiMnO_6$ and $La_2CoMnO_6$ Films Grown on $SrTiO_3(100)$

***H. Geisler****, C.A. Ventrice,* Texas State University*, Y. Losovyj,* Louisiana State University*, K. Chetry, A. Gupta*, University of Alabama

The surface electronic structure of thin films of the double perovskites $La_2NiMnO_6$ and $La_2CoMnO_6$ have been measured using ultra-violet photoelectron spectroscopy at the CAMD synchrotron. Both $La_2NiMnO_6$ and $La_2CoMnO_6$ are magnetic semiconductors with magnetic transition temperatures in their bulk phases of 280 K and 226 K, respectively. The thin films were grown on $SrTiO_3(100)$ substrates using pulsed laser deposition. To prepare the clean surfaces before photoemission measurements, the samples were sputtered with 1 keV Ar ions and annealed at ~400 °C in an $O_2$ atmosphere of $10^{-6}$ Torr. Angle-resolved photoemission measurements of both surfaces show very little dispersion of the valence emissions. Annealing the surfaces in ultra-high vacuum results in a shift of the valence features away from the Fermi level, indicating that loss of surface oxygen results in an n-type doping of these surfaces.

### SS-TuP4 X-ray Photoelectron Study of Polycrystalline Samples Type $SeCuO_3$ and $SeMnO_3$ Perovskites

***L. Huerta****, R. Escamilla,* Universidad Nacional Autónoma de México*, M. Flores,* Universidad de Guadalajara, México*, E. Morán, M. Alario-Franco*, Universidad Complutense, España

Polycrystalline samples type $SeCu_{1-x}Mn_xO_3$ perovskites were studied by x-ray photoelectron spectroscopy (XPS). The XPS spectra revealed Se, Cu and Mn oxides on the surface of the samples, mainly $SeO_2$, CuO and MnO. After with great periods of etching time the intensity of $SeO_2$, CuO and MnO decreased. The Se 3d, Me $2p_{3/2}$ (Me = Cu, Mn), Me 3d and O 1s spectral lines associated to the chemical states $SeMO_3$ were identified and they do not change with increased of etching time.

### SS-TuP5 A STM Study of Pt Nanoparticles Deposited on $CeO_x(111)$ Thin Films

***P.J. Riedel****, J. Zhou*, University of Wyoming

Ceria-supported Pt nanoparticles are widely used in many important applications, including three-way automobile emission-control catalysis and fuel cells owing to the peculiar redox properties and oxygen storage capacity of ceria as well as the synergistic effect between the Pt and ceria. Previous chemistry studies using XPS and TPD in the literature have demonstrated that the reactivity of ceria-supported Pt nanoparticles is dependent on the cerium oxidation state. To elucidate the nature of their reactivity, we investigated their structure and morphology using STM. Reducible $CeO_x(111)$ thin films were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Our data demonstrate that surface structures of ceria thin films are dependent on the degree of ceria reduction. Fully oxidized $CeO_2(111)$ film exhibits a fairly low density of point defects due to the formation of oxygen vacancies. However, the number of surface defects increases as the ceria film is reduced. Pt particles were vapor-deposited onto ceria thin films at 300 K. The growth of Pt particles was investigated by STM as a function of metal coverage, post-deposition annealing temperatures, as well as Ce oxidation state, which were further compared to the growth of Rh and Pd. The research is sponsored by the start-up fund at the University of Wyoming and the Wyoming NASA Space Grant.

### SS-TuP6 Growth and Reactivity of Pt-Au Bimetallic Nanoclusters Supported on $TiO_2(110)$

***J.S. Ratliff****, J.B. Park, S.A. Tenney, S.F. Conner, D.A. Chen*, University of South Carolina

Pure Pt, pure Au, and bimetallic Pt-Au clusters were deposited on $TiO_2(110)$ at room temperature and studied with scanning tunneling microscopy, low energy ion scattering, and temperature programmed desorption. Pt forms smaller clusters with higher cluster densities than Au for the same metal coverage. Bimetallic Pt-Au clusters were formed by seeding Au at existing Pt clusters. The growth of Au on Pt seed clusters was confirmed by a decrease in cluster density upon dosing Au onto 0.25 monolayers (ML) of Pt. For the growth of Au on Pt seed clusters, the average cluster size increases and cluster density decreases with increasing Au coverage. Low energy ion scattering spectroscopy confirms that both Pt and Au are at the surface of the clusters, even at 300K. Carbon monoxide was used to probe the activity of the bimetallic clusters. With a constant total metal coverage, CO desorption scales linearly with the Pt percentage. Upon dosing increasing amounts of Au onto 0.25ML of Pt, CO desorption decreases but does not reach zero, even with 3ML of Au, suggesting that CO may be able to pull Pt to the surface of the clusters. $CO_2$ production from bimetallic clusters exposed to $O_2$ prior to CO exposure decreases much more rapidly with increasing Au coverage than does CO desorption due to decreased number of Pt surface sites for $O_2$ dissociation.

### SS-TuP7 Temperature Program Desorption Study of $Cu_x$ on Reduced $TiO_2(110)$

***J.C. Lofaro, Jr.****,* Stony Brook University*, M.G. White*, Brookhaven National Laboratory and Stony Brook University

Copper catalysts supported on metal oxides have been used as a heterogeneous catalysts in industrial setting for various chemical processes.[1,2] Recent works have shown that copper nanoparticles supported on metal oxides (ZnO, $CeO_2$, $TiO_2$) have higher activity for the water gas shift reaction (WGSR) as well as other chemical processes.[3,4] Here, copper nanoparticles are deposited on a $TiO_2(110)$ single crystal using a homemade thermal evaporator, which is used as a model system. Auger electron spectroscopy (AES) is used to characterize the copper coverage and temperature programmed desorption (TPD) is used to probe the clusters reactivity and thermal stability. Copper coverages ranging from 0.25ML to 10ML are investigated. Probe molecules including carbon monoxide and water since those are the starting points for the WGSR, which copper is known to catalyze at high temperatures.[5]

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### SS-TuP8 Photooxidation of Acetone and Butanone on Rutile $TiO_2(110)$

***D.P. Wilson****, D. Sporleder,* Stony Brook University*, M.G. White*, Stony Brook University, Brookhaven National Laboratory

Interest in the photooxidation of organic compounds on heterogeneous surfaces such as $TiO_2$ has increased in recent years. Here, acetone and butanone, two common organic ketones, are studied under UHV conditions to determine what fragmentation occurs during photooxidation and to gain insight as to the predictability of desorbing species. The data was collected using a pump-probe time-of-flight (TOF) method. Excitation occurs via exposure to 3.7 eV photons followed by ionization with 13.05 eV photons. Preheating the surface to ~200K facilitated the formation of an organic-diolate species needed for photoactivity. During butanone photooxidation, different desorption mechanisms between mass 30 and masses 27-29 are evident. Background thermal results and preliminary translational energy distributions are calculated for acetone and some butanone fragments and are presented here.

### SS-TuP9 Significant Reduction in Adsorption Energy of CO on Platinum Nanoparticles on Graphite

***J.P. Oh****, T. Kondo,* University of Tsukuba, Japan*, Y. Suda,* Toyohashi University, Japan*, D. Sekiba, H. Kudo, J. Nakamura*, University of Tsukuba, Japan

Adsorption and desorption of CO on Pt vapor-deposited on highly oriented pyrolytic graphite (HOPG) have been investigated by temperature programmed desorption (TPD) of CO and in-situ helium atom scattering (HAS). Pt particles deposited on HOPG with sub-monolayer coverage are found to exhibit lower temperature desorption peak of CO at ~300 K at a heating rate of 0.5 K/sec. With increasing Pt coverage on HOPG, the desorption peak of CO at 450 K becomes dominant as observed on Pt single crystals. It was confirmed by Rutherford backscattering spectroscopy (RBS) measurements that any impurities other than carbon and Pt do not exist in the HOPG sample. These results indicate that the Pt particles deposited on a graphite surface with sub-monolayer coverage has significantly different properties for CO adsorption from that of Pt single crystal: lower adsorption energy of CO on Pt of Pt/HOPG than that for Pt single crystal. The reduction in the adsorption energy has been attributed to the interface interaction between Pt particles and graphite surface based on the separately conducted scanning tunneling microscopy experiment. Simultaneous measurement of HAS with CO-TPD indicated, the morphological change of the specific Pt particles at ~350 K. Scanning electron microscope observation before and after annealing the Pt/HOPG sample also reveals that Pt particle is mobile at higher temperatures above 350 K. However, sintering of Pt leading to an increase of particle size was not observed.

**SS-TuP10 Low-Temperature Reaction of $Cl_2$ and $C_2H_4$ on ZnO(000-1) Single Crystal Surfaces*, W.H. Doh*,** *C.M. Kim*, Kyungpook National University, South Korea

We studied the reaction of $Cl_2$ and $C_2H_4$ co-adsorbed on ZnO single crystal surfaces. It is observed that $C_2H_4$ is molecularly adsorbed on ZnO at 110 K and desorbed intact from the surface when the surface temperature is increased. $Cl_2$ is molecularly adsorbed on ZnO at 110 K and decomposed to atomic chlorine when the surface is heated to higher than 200 K. When the ZnO surface is co-adsorbed with $Cl_2$ and $C_2H_4$, desorption of 1,2-dichloroethane is observed. We studied the mechanism of low-temperature addition of Cl to $C_2H_4$ on ZnO. We propose that "hot" atoms are produced in the process of $Cl_2$ dissociation and these "hot" chlorine atoms attack co-adsorbed $C_2H_4$ to produce 1,2-dichloroethane before thermodynamic equilibrium is reached.

**SS-TuP11 Effect of $Al_2O_3$ and $ZrO_2$ Supports on Rh for Reaction Properties of NO*, I. Nakamura*,** *A. Takahashi, T. Fujitani*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

The reduction of the noble metal content in the three-way automotive catalyst (Rh, Pt, Pd/$Al_2O_3$-$ZrO_2$-$CeO_2$) is currently required. In order to reduce noble metal loading, the enhancement of atomic efficiency and suppression of oxidation and sintering of noble metal are important subjects. To overcome these subjects, the clarification of the supported metal state is necessary. In this study, we investigated the influence of oxide support on the structure of Rh and the NO reactivity using the Rh/$Al_2O_3$ and Rh/$ZrO_2$ model catalysts. The model catalysts were prepared by deposition of Rh onto the $Al_2O_3$ and $ZrO_2$ thin films. The NO dissociation activity on the Rh/$Al_2O_3$ model catalyst was higher than that on Rh(111). In contrast, the activity for the Rh/$ZrO_2$ model catalyst was the same as Rh(111). Furthermore, the dissociation activity on the Rh/$Al_2O_3$ model catalyst increased by heating, but no enhancement by heating treatment was observed for the Rh/$ZrO_2$ model catalyst. We thus considered that the $Al_2O_3$ support promotes the NO dissociation activity by changing the Rh surface structure. To clarify the effect of $Al_2O_3$ support on Rh, we examined the NO adsorption state on the model catalysts. The IRAS peak due to NO adsorbed on bridge site was observed at 1645 cm$^{-1}$ for the Rh/$Al_2O_3$ model catalyst. For the Rh/$ZrO_2$ model catalyst, the peak was seen at 1616 cm$^{-1}$, which was attributed to NO on hollow site. These results indicate that the surface structures of Rh are (100) and (111) faces for the Rh/$Al_2O_3$ and Rh/$ZrO_2$ model catalysts, respectively. We also confirmed that the exposed surfaces of Rh supported on $Al_2O_3$ and $ZrO_2$ are the (100) and (111) face from a comparison with the rate and apparent activation energy for NO dissociation on Rh(100) and Rh(111). Thus, we found that the effect of $Al_2O_3$ support on Rh for an enhancement of NO dissociation activity is to stabilize the surface structure of the (100) face with a high NO dissociation ability. AFM measurements confirmed that the small Rh particles with 2.5 nm diameter were formed on the Rh/$Al_2O_3$ model catalyst. We concluded that the $Al_2O_3$ support affected the morphology of the Rh surface by stabilization of small Rh particle, resulting in the enhancement of NO dissociation activity.

**SS-TuP12 Au-N Synergy and N-Doping of Metal Oxide-Based Photocatalysts*, J. Graciani*,** *A. Nambu,* Brookhaven National Laboratory, *J. Evans,* Universidad Central de Venezuela, *J.A. Rodriguez,* Brookhaven National Laboratory, *J.F. Sanz*, Universidad de Sevilla, Spain

N-doping of titania makes possible photocatalytic activity for the splitting of water, and other reactions, under visible light. Here we show from both theory and experiment that Au preadsorption on TiO2 surfaces significantly increases the reachable amount of N implanted in the oxide. The stabilization of the embedded N is due to an electron transfer from the Au 6s levels toward the N 2p levels, which also increases the Au-surface adhesion energy. Theoretical calculations predict that Au also can stabilize embedded N in other metal oxides with photocatalytic activity such as SrTiO3 and ZnO, producing new states above the valence band or below the conduction band of the oxide. In experiments, the Au/TiNxO2-y system was found to be more active for the dissociation of water than pure TiO2 or TiO2-y. Furthermore, the Au/TiNxO2-y surfaces were able to catalyze the production of hydrogen through the water-gas shift reaction (WGS) at elevated temperatures (575- 625 K) displaying a catalytic activity superior to that of pure copper (the most active metal catalysts for the WGS) or Cu nanoparticles supported on ZnO.

**SS-TuP13 Bimetallic Pt/Metal Nanocatalysts for the Decomposition of Methanol: Effect of Secondary Metal on Oxidation State, Activity, and Selectivity*, J.R. Croy*,** *S. Mostafa, L. Hickman, H. Heinrich, B. Roldan Cuenya*, University of Central Florida

Bimetallic Pt-Metal (Pt-M) catalysts are important in a wide range of applications including the direct methanol fuel cell (DMFC). In order to take full advantage of Pt/M systems in the design of new and efficient nanocatalysts, we must understand the structural, chemical, and electronic modifications brought about by the addition of the secondary metal M. We present here an investigation of the influence that the addition of secondary metals (M=Au, Pd, Ru, and Fe) has on the oxidation state, activity, and selectivity of $ZrO_2$-supported Pt nanoparticles. We use as a probe reaction the decomposition of MeOH. Size-selected bimetallic Pt nanoparticles were obtained by diblock-copolymer encapsulation and deposited on nanocrystalline $ZrO_2$ powder. The chemical composition of the particles was studied by X-ray photoelectron spectroscopy and structural characterization was done by atomic force microscopy and transmission electron microscopy. The reactivity of the bimetallic systems for MeOH decomposition was monitored in a packed-bed mass flow reactor by mass spectrometry. Distinct atomic segregation trends were observed upon annealing these nanoparticles in an oxygen-rich environment. The affect these trends have on the oxidation state of Pt and how this state influences reactivity will be discussed.

**SS-TuP14 Reaction Properties of $O_3$ and CO Over Gold Surface*, T. Fujitani*,** *I. Nakamura, A. Takahashi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

Gold nanoparticles supported on $TiO_2$ exhibit high catalytic activity for CO oxidation. Although numerous investigations have been carried out to elucidate the source of this enhanced activity, there are still controversies concerning the active sites and the role of support for the Au/$TiO_2$ catalyst. In addition to the aforementioned studies, reactions of $O_2$, $O_3$ and CO on gold surfaces have been investigated by means of surface science techniques. Recently, we found that $O_3$ dissociation and CO adsorption depend strongly on the gold surface structure. Here, we report the adsorption and desorption properties of atomic oxygen produced from $O_3$ exposure and CO adsorption properties on gold single crystals as well as gold deposited on $TiO_2$(110). XPS measurements confirmed that no dissociative adsorption of $O_2$ occurred on surfaces of Au(111), Au(100) and Au(311). On the other hand, atomic oxygen was observed on Au(111) and Au(311) upon exposure to $O_3$, but no atomic oxygen was detected on Au(100). The saturation coverage of atomic oxygen on Au(311) was half of that observed on Au(111), where the exposed (111) face on Au(311) was half of that on Au(111). Furthermore, the initial formation rate of atomic oxygen for Au(311) was half of that for Au(111). These results clearly indicate that $O_3$ dissociation over gold surfaces proceeded selectively on the (111) face. We found that the adsorption behavior of CO also depended on the gold surface structure. PM-IRAS peaks of CO at 2070-2080 cm$^{-1}$ were observed for Au(111) and Au(100) at CO pressures above 0.5 Torr; these peaks were assigned to the CO adsorbed on atop sites (atop-CO). In contrast, the peak due to atop-CO adsorbed on step sites was seen at 2117 cm$^{-1}$ for Au(311) at 0.01 Torr. It was thus shown that the step sites on the gold surface were effective for CO adsorption under low CO pressure. Next, we investigated the CO adsorption state for the gold nanoparticles on $TiO_2$(110). PM-IRAS peak of CO adsorbed on atop sites of gold atom was observed at 2120 cm$^{-1}$, which was higher than the frequency of the CO adsorbed on Au(111). The CO frequency observed for the Au/$TiO_2$ model catalyst agreed with that on step sites for Au(311). We thus found that the $TiO_2$ support influences the electronic state of the supported gold, resulting in the formation of positively charged gold nanoparticles.

**SS-TuP15 Formation and Thermal Stability of Gold Oxide and Platinum Oxide Shells on Nanoparticles: Size and Support Effects*, L.K. Ono*,** *J.R. Croy, B. Roldan Cuenya*, University of Central Florida

Gold and Pt nanoparticles (NPs) with two different size distributions (average sizes of ~1.5 and ~5 nm) have been synthesized by inverse micelle encapsulation and deposited on reducible ($TiO_2$) and non-reducible ($SiO_2$, $ZrO_2$) supports. The thermal stability of oxidized Au and Pt species formed upon cluster exposure to atomic oxygen has been investigated in ultrahigh vacuum using a combination of temperature-, time- and CO dosing-dependent X-ray photoelectron spectroscopy (XPS), as well as temperature programmed desorption (TPD). Our work on gold clusters demonstrates that (a) low temperature (150 K) exposure to atomic oxygen leads to the formation of surface, as well as sub-surface gold oxide, (b) the presence of the reducible $TiO_2$ substrate leads to a lower gold oxide stability compared to that on $SiO_2$, possibly due to a $TiO_2$ oxygen vacancy-mediated decomposition process, (c) heating to 550 K (Au/$SiO_2$) and 300 K (Au/$TiO_2$) leads to a near-complete reduction of small (~1.5 nm) NPs while a partial reduction is observed for larger clusters (~5 nm), and (d) the desorption temperature of $O_2$ from pre-oxidized Au clusters deposited on $SiO_2$ depends on the cluster size, with smaller clusters showing stronger $O_2$ binding. Preliminary data on the formation and thermal stability of different Pt oxide species ($PtO_2$ and PtO) on size-selected Pt clusters will be shown. Emphasis will be given to how the nature of the oxide support affects this stability. Furthermore, the distinct reactivity of similarly-sized, pure Pt and Au nanoparticles versus their oxidized counterparts will be discussed.

**SS-TuP16 3D Concentration and Structure Maps of Heterogeneous Surfaces Determined by LEEM-IV Analysis***, J. Sun**, University of New Hampshire*, J.B. Hannon,* IBM T. J. Watson Research Center*, G.L. Kellogg,* Sandia National Laboratories*, K. Pohl*, University of New Hampshire

Controlling compositional heterogeneity is important in ultrathin films growth, but determining exactly how and why heterogeneity develops is extremely challenging. The reason is that the three-dimensional compositional and structural profile of the film is difficult to measure because of the lack of surface techniques that combine high spatial resolution, subsurface sensitivity, chemical identification capability and high temporal resolution. For example, STM is not sensitive to the subsurface region and LEED averages over a large surface area. To overcome these limitations, we have developed a novel analysis approach[1] that allows us to measure the evolution of the 3D compositional and structural profile of a heterogeneous alloy surface in real time. We do this by quantitatively analyzing the pixelated intensity in the low-energy electron microscopy (LEEM) images. In the dynamical IV (intensity-vs.-voltage) analysis, a proper model for the inner potential, representing the atomic muffin-tin constant and the inelastic optical scattering, was adapted to overcome the challenges in very low-energy electron scattering. The structural and non-structural parameters are optimized simultaneously in search of the real surface structure that gives a best fit between the calculated and experimental IV curves. We have measured the composition of a CuPd surface alloy in the three topmost atomic layers, during growth, with 8.5 nm lateral resolution and monolayer depth resolution. From the 3D compositional and structural profiles, we have identified a generic step-overgrowth mechanism that leads to inherent alloy heterogeneity at steps. The heterogeneity can be traced to the difference between bulk and surface diffusion of Pd. Furthermore, Monte Carlo simulations are described to reproduce the time evolution of the compositional heterogeneity and give support to the step-overgrowth model. By the LEEM-IV analysis technique, the surface structural and compositional information measured in situ can be correlated with other surface properties, such as surface strain, diffusion mechanisms, and growth and decay processes. This work is supported by the National Science Foundation, the Department of Energy, Office of Basic Energy Sciences, and the Petroleum Research Fund.

[1] Sun, J., Hannon, J. B., Kellogg, G. L. & Pohl, K., Phys. Rev. B 76, 205414 (2007); Hannon, J. B., Sun, J., Pohl, K. & Kellogg, G. L., Phys. Rev. Lett. 96, 246103 (2006).

**SS-TuP17 Reactivity of Diatomic Molecule on Bimetallic Surface: The Case of $O_2$ Adsorption and Dissociation on Pt/Fe***, M.C.S. Escano††, H. Kasai*, Osaka University, Japan

Bimetallic surfaces have been receiving increasing catalytic interest. Aside from using strain to tune reactivity, to a large extent, metal overlayers exhibit modified surface electronic structure due to interfacial interactions.[1,2] While dissociative adsorption of small molecules on metal surfaces has been studied extensively, theoretical studies on gas-bimetallic surface interaction have been sparse. Previous ab-initio calculations on atomic and electronic structure of Pt/Fe(001) show small lattice mismatch and a charge transfer from Pt and Fe atom sites towards Pt-Fe interface.[3] Layer by layer density of states curves against Pt(001) and Fe(001) show increase of d states at the Fermi level and a spin polarization of Pt $d_{zz}$ states. Such changes with respect to the pure components call for investigation on $O_2$ surface reactivity. Spin-polarized density functional theory calculations were performed to investigate adsorption and $O_2$ dissociation on Pt/Fe(001). The adsorption characteristics of atomic and molecular oxygen are compared with clean Pt(001). The energetics of $O_2$ adsorption and dissociation are discussed in terms of two-dimensional cuts of the six-dimensional potential-energy surface. Results show "no barrier" $O_2$ molecule preferential adsorption on bridge with O-O axis directed towards top sites (t-b-t). A barrierless dissociation over one trajectory, O-O axis parallel and spanning over bridge-hollow-bridge (b-h-b) site, is also predicted. The potential energy decreases monotonically along this lowest energy reaction path indicative of strong $O_2$ interaction with the surface. A proposed pathway for dissociation may take molecular adsorption along t-b-t and a translation and dissociation towards b-h-b. Detailed analysis of the transition state reveals ease of translation towards the b-h-b. Local density of states (LDOS) of $O_2$ arriving over bridge for the molecular state and at the transition state support strong hybridization between $O_2$ $p_x$-states and Pt $d_{zz}$ states. In the meeting, we will detail the mechanism of $O_2$ reactivity based on charge redistribution, total charge flow integrals and partial charge density plots.

[1] M. Mavrikakis, B. Hammer and J.K. Nørskov, Phys. Rev. Lett. 81, 2819 (1998).

[2] J.A. Rodriguez, Surf. Sci. Rep. 24, 223 (1996)

[3] MC Escaño, H. Nakanishi and H.Kasai, J. Phys.: Cond. Matt. 19, 482002 (2007).

## Vacuum Technology
## Room: Hall D - Session VT-TuP

## Poster Session, Including Student Poster Competition

**VT-TuP1 Construction of a Laboratory Based Resistance Thermal Evaporator and/or Sputtering Module and the Associated Safety Systems***, V. Lambe, A. Pender*, Institute of Technology Tallaght, Ireland

Construction of a laboratory based resistance thermal evaporator and/or sputtering module and the associated safety systems. This student project involves building both the vacuum system consisting of bell jar, turbo and rotary vein pump and associated ducting and valves. The high voltage system consists of a 30A dc power supply and associated circuitry. The aim of the project was to evaporate and characterise aluminium deposition on silicon (thickness versus time, power versus thickness etc). An addition aim was to characterise the equipment and provide documentation for the user. A simple film thickness monitor is to be built and installed into the system. In particular the student has concentrated on the safety aspects of the design. These includes, 1. Half atmosphere switch to protect the turbopump 2. EMO and breaker circuitry for the high voltage power supply 3. Interlocks for the power supply 4. Air driven vacuum interlock to protect against high voltage.

**VT-TuP5 A Novel, UHV Analysis System for Detecting Electron Stimulated Reaction Products Generated during Field Emission Studies***, M. Bagge-Hansen, R.A. Outlaw, M.Y. Zhu, H. Chen, D.M. Manos*, The College of William and Mary

Carbon nanosheets (CNS) are a promising carbon allotrope for high current field emission cathodes and are grown by plasma-enhanced chemical vapor deposition (PE-CVD) from a $C_2H_2/H_2$ gas blend at substrate temperatures of ~ 600 °C. The resulting film consists of $sp^2$, vertically oriented, honeycomb carbon arrays terminating in a single graphene sheet that serve as field emission cathodes. A novel ultrahigh vacuum (UHV) system has been assembled for the study of gas products generated by etching of the CNS during field emission testing. A residual gas analyzer (RGA) located in direct line-of-sight of the field emission gap (254 µm) of the Cu diode geometry is used for measurement of reaction products generated during field emission tests. Electron bombardment of the Cu anode (up to 2 $mA/mm^2$) generates atomic hydrogen (1-5 eV) by electron stimulated desorption (ESD) which, in turn, reactively etches the CNS cathode and produces predominantly $CH_4$ as a reaction product. The Cu anode assembly is actively water-cooled by an external chiller to 0 °C to minimize thermal effects. The typical operating pressure is $<2x10^{-10}$ Torr. Mass spectral and I-V data are collected simultaneously by an integrated LabView program. Carbon monoxide and carbon dioxide were also observed during field emission and are also correlated with the emission current. Scanning electron microscopy of the CNS topography and cross section was used to confirm the etching rate (~2 nm/hr). These results are consistent with the density functional predictions reported by Kanai et al. of $CH_4$ generated by atomic hydrogen incident on graphene.[1]

[1] C. Kanai, K. Watanabe, and Takakuwa, Phys. Rev B 63, 235311 (2001).

**VT-TuP6 A Compact Deposition Chamber Design for Low Temperature Growth of Ultra-Thin Crystalline Films on Metal-Insulator-Semiconductor Devices***, R.E. Lake, J.R. Puls, M.P. Ray, C.E. Sosolik*, Clemson University

Fabricating ultra-thin crystalline metal films is especially important in new studies of ballistic electron transport at interfaces and energetic processes of atoms on surfaces. In order to probe physics at the atomic level without contamination these studies require that homogeneous, atomically ordered, and defect free thin films be deposited in the same ultra-high vacuum (UHV) system where they will be studied. With this constraint in mind, we have designed and built a compact deposition chamber that allows for in situ growth and analysis of atomically ordered epitaxial metal layers which are only a few monolayers thick. This UHV deposition chamber is attached to a port on the fast exchange load lock (FELL) of our Omicron variable temperature STM (VT-STM) and has an internal volume of 476 $cm^3$. It contains an evaporation gun slot that can be equipped with either an electron beam evaporator or a simple thermal evaporator. The target substrates used for deposition are compatible with the VT-STM design and are held in place at the center of the deposition chamber in a specially-designed clamping slot fabricated into an oxygen-free high-conductivity copper stage. The copper sample stage facilitates rapid cooling of the substrates to the temperatures required for crystalline film growth. This is done using a continuous flow of liquid nitrogen through the hollowed out interior of the sample stage. Following film growth, samples can be kept under vacuum and transferred into the FELL via a rotary-linear manipulator and then directly into the VT-STM chamber for analysis. Our compact

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* Morton S. Traum Award Finalist

chamber design has made the VT-STM system more effective for measurements of as-grown surfaces and interfaces, and its low cost and ease of use should be of special interest to other physicists, chemists, and engineers with similar research goals.

**VT-TuP7 HORST - A New Device for Digital In-Line X-ray Holography**, ***F. Staier***, *A. Rosenhahn*, *M. Grunze*, University of Heidelberg, Germany

The holographic x-ray scattering chamber (Holographische Röntgenstreukammer HORST) is a new experimental station for coherent x-ray sources such as synchrotrons and free electron lasers. It is designed for digital in line holography but also flexible to have add ons like magnets or beamstops for diffraction imaging. HORST consists of a large vacuum chamber with three stage systems for pinhole, sample and camera positioning and a differential pumping stage to achieve a very good vacuum pressure at the beamline. All this is mounted on a mobile and height adjustable framework. The three motorized stage systems has 13 axes of motion: pinholes can be moved and tilted perpendicular to the beam axis, samples can be moved in all three dimensions as well as rotated for tomography and the CCD camera can be positioned. We present first images acquired at UE52SGM at BESSY which characterizes the imaging properties of the system. The applicability to handle biological samples and first holotomography results will be presented.

**VT-TuP9 Scaling of Low-Pressure Transport Coefficients for Gas Mixture Flow in a Tube**, ***M. Vukovic***, Tokyo Electron, US Holdings

Low pressure gas mixture flow in a tube can be analyzed with the linearized Boltzmann equation or the DSMC method. Alternatively, one can use the linearized Boltzmann equation to calculate gas transport coefficients that depend on the local concentration and density. These coefficients are then used in the gas flow analysis. This procedure requires repeated solution of the linearized Boltzmann equation, or preparation of coefficient tables for the whole range of expected gas concentrations and densities. Using the numerical results of Sharipov and Kalempa (J. Vac. Sci. Technol. A 20, 814 2002), we show how to rescale each transport coefficient for a gas mixture, collapsing the curves for various gas mixtures to a single curve. Once this re-scaling is done, to calculate the transport coefficients one needs the free-molecular value of the coefficient, the slip flow value, and interpolation of the dimensionless curve. This reduces the computational cost of the coefficient calculation to that of calculating the slip flow coefficients (for which relatively inexpensive methods are available) and interpolation of the dimensionless curves.

**VT-TuP10 Vacuum Pressure Simulation for the Upgrade of Front-End at NSLS Insertion Device Beamline**, ***J.-P. Hu***, Brookhaven National Laboratory

The beamline 9 at X-ray storage ring of the Brookhaven Lab's National Synchrotron Light Source (NSLS) is being upgraded from a conventional bending magnet beamline to an insertion device beamline, with installation of a mini-gap undulator (MGU) at upstream of the dipole magnet. The new undulator, which is made of neodymium-iron-boron magnet and vanadium-permandur poles, will generate a high-brightness photon beam through the X-9 front-end to the experimental end-station enclosure, where sampling of nano materials will be conducted by small-angle X-ray scattering (SAXS). For the beam focusing and radiation shielding, most of the optical apparatus and vacuum systems at front-end of the beamline will be modified or replaced. To determine limit of conductance for gas pumping between the proposed aperture and collimator where the beam size is defined, vacuum pressure along the straight chamber from beam port of the undulator down to the differential pump (replacing beryllium window as vacuum barrier) is calculated, using two validated computer codes. In the statistical Molflow code which is a Monte-Carlo based software package, chamber conductance through different sections at front-end is estimated for pump arrangement. In the analytical Vaccalc code which is a finite-difference formulated Fortran program, pressure distribution along the beam axis is calculated based on balanced diffusion-and-pumping of gas species in consecutive segments of the vacuum chamber. The result is verified by the output from code runs previously performed to optimize the beamline vacuum. Details of pressure profile versus component setup at X-9 front-end will be presented. (Work performed under auspices of the United States Department of Energy, under contract DE-AC02-98CH10886).

**VT-TuP11 Thermistor Vacuum Gauge; High Sensitivity Shows Direction and Acceleration Which Enables Vacuum Leak Detection**, ***D. Casilio***, *R. Kromer*, Myers Vacuum

Thermistor gauge sensors are rugged sensors that have been used to measure vacuum indirectly for many decades. The single resistor element is employed in a bridge-type detector. A constant source to the heating element of the sensor is maintained to a fixed resistance. The amount of drive needed to maintain this value is measured. A decrease in pressure reduces the number of gas molecules available to transfer heat away from the heating element. This results in a temperature and resistance output change from the sensor. This signal is filtered and amplified, and then sent to an analog to digital converter. The microprocessor reads this signal, does further filtering and uses the result as an index into a lookup table for pressure. This value is written to the display and to a digital to analog converter that generates the analog voltage output. High sensitivity over most of its range allows for direction indication as well as how fast pressure is accelerating in which direction. Due to its quick response, a solvent can be used to trigger the response near a chamber vacuum leak.

## Applied Surface Science
## Room: 207 - Session AS-WeM

## Advanced Data Analysis for Surface Characterization
**Moderator:** S. Pachuta, 3M

8:00am **AS-WeM1 Near Real-time Analysis of XPS Data**, ***A.S. Lea***, *D.R. Sisk, M.H. Engelhard,* Pacific Northwest National Laboratory, *J.E. Castle,* University of Surrey, UK, *D.R. Baer*, Pacific Northwest National Laboratory

The application of x-ray photoelectron spectroscopy (XPS) to analyze different types of materials appears to be growing rapidly around the world. In our Department of Energy National User Facility the Environmental Molecular Sciences Laboratory (EMSL) we currently have user requests for thousands of hours per year of XPS based experiments and more routine sample analysis. The real-time (or near real-time) analysis of the XPS data as it is collected has significant potential advantages to scientists and instrument operators in that it has the potential to qualitatively alter the way experiments are done. Such endeavors have the potential, not only to improve the turn-around time for data analysis and the sophistication of data analysis reportable to the User, but also to reduce the labor involved in data analysis, resulting in significant time (and cost) savings. We are developing a prototypical real–time data analysis capability to analyze x-ray photoelectron spectroscopy (XPS) data generated in EMSL. Our goals are to provide atomic composition, carbon contamination layer thickness and component segregation (layer) information as soon as adequate data is collected on a specimen. Because of the high user need and previous efforts to design an XPS expert system, XPS is a good candidate for development of a near real time data analysis capability. Our real-time data analysis package follows many elements of the expert system approach proposed by Castle.[1] A set of rules and algorithms are used to address a well defined series of analysis objectives (based on the needs of the XPS analysis) to characterize the surface in terms of atomic concentration, layer sequences, and enrichment/depletion of elements as a function of depth. For each goal, rules have been developed to determine whether the stated goals are met. The real-time analysis package evaluates the rules by automated interpretation of the wide-scan (survey) spectra. Once the goals have been met, the real-time analysis package generates a report that includes, in addition to the above stated goals: a first level approximation of surface composition and metadata associated with this analysis, which will be stored with the datafile produced by the data analysis package.

[1] Castle, J.E., J. Vac. Sci. Technol. A (2007) 25, 1-27.

8:20am **AS-WeM2 Data Scaling for Quantitative Imaging XPS**, ***J. Walton***, The University of Manchester, UK, *N. Fairley*, Casa Software

Multivariate analytical techniques are seeing increasing use in surface analysis due to the ability of current instrumentation to acquire multispectral data sets. Their use can provide a significant improvement in signal/noise, and simplify analysis of the large amount of data present by reducing its dimensionality. In the case of XPS this enables quantification by measurement of photoelectron peak areas, and chemical state determination using curve fitting to the spectrum at every pixel in an image. Selection of the most appropriate technique is dependent upon the characteristics of the data, and for XPS, where there are relatively few components compared with the number of objects in the data set, Non-linear Iterative Partial Least Squares (NIPALS) affords a significant saving in computational requirements, as the procedure may be terminated after the appropriate number of components has been calculated. A key aspect in the use of these techniques is their ability to order the data so that the chemical information is easily separated from the noise. For data acquired by pulse counting, which is governed by Poisssonian statistics and where the variance scales as the data, ordering the data by variance may result in noise from high intensity photoelectron peaks dominating low intensity chemical information. Effective separation of noise and chemical information therefore necessitates prescaling the data, so that the noise is evenly distributed. Individual objects, whether images or spectra, may be scaled by the square root of the variance. This provides good separation of the chemical information from the noise, but leads to a signal level below which information cannot be extracted. This is not important where the inelastic background is greater than this base level, but leads to significant errors in quantification where the background is equal to, or below this level, and data is lost from photoelectron peaks. This is particularly important for photoelectron peaks occurring at low binding energy. It will be shown that scaling to the square root of the mean variance in both image and spectral domains, known as optimal scaling, avoids this limitation and allows use of the NIPALS procedure for fully quantitative imaging XPS.

8:40am **AS-WeM3 Using Multivariate Analysis and Modeling for Structure-to-Property Relationships Built from XPS Data**, ***K. Artyushkova***, *J.E. Fulghum, P. Atanassov*, The University of New Mexico **INVITED**

This talk will discuss new approaches in accelerating material development and design by building models describing structure-to-property relationship based on X-ray Photoelectron data. The science of designing of heterogeneous materials has benefited from an understanding of the chemical, surface and materials phenomena at the nanoscale. Among the more complex nano-structured functional materials that will be discussed in this talk are electrocatalysts and biocatalysts. Understanding the structure of catalysts, and linking this structure to performance is essential for identification of the active catalytic sites, for optimization of catalyst performance, and elucidation of failure mechanisms. XPS is one of the most widely utilized surface spectroscopic techniques for analysis of catalyst structure. The ability to discriminate between different surface oxidation states and chemical environments is one of the primary advantages of the use of XPS in the characterization of catalyst structures. It is critical that the XPS spectra are interpreted and quantified with a high confidence level, as this information will be a central link between structure and performance. Although, the majority of XPS analyses of catalysts are focused on identifying the oxidation state and overall speciation, the ambiguity in peak assignment from overlapping peak components in XPS spectra is still a significant problem. Multivariate statistical methods of data analysis (MVA) are of critical importance in developing unambiguous methods of XPS data interpretation. Correlation of XPS structural data to any other property, such as derived from BET porosity, microscopic images and performance characteristics, represents a multivariate problem. Initially, Principal Component Analysis and Correlation maps will be used to study qualitative correlations between amounts of chemical species detected by XPS and variety of relevant for particular system macroscopic properties such as surface area, pore size distribution, electrochemical performance, corrosion rate, etc. In order to learn about relationship between several independent variables and a dependent variable and to determine the magnitude of those relationships, a variety of Regression Models are widely used. Multiple Linear Regression along with Genetic Algorithm for Variable selection will be discussed in attempt to build a predictive model between XPS, macroscopic parameters and performance characteristics.

9:20am **AS-WeM5 Identification and Quantification of ToF-SIMS Images with Topography using Multivariate Analysis**, ***J.L.S. Lee***, *I.S. Gilmore,* National Physical Laboratory, UK, *I.W. Fletcher,* Intertek MSG, UK, *M.P. Seah*, National Physical Laboratory, UK

Surface topography is a crucial issue for the analysis of many innovative devices such as microfluidic systems, fibres, composite materials, sensors, organic electronics and biomedical devices. The strength and durability of these components is critically dependent on their nanoscale surface chemistry and molecular interactions. However, quantitative characterisation of surfaces with topography remains a significant challenge due to the lack of systematic and validated measurement and data analysis methods. Previously, we presented a systematic study of the effects of surface topography on ToF-SIMS and provided guidance to practical analysts for identifying and reducing topographical effects.[1] Here, we investigate the robust use of multivariate methods for the identification and quantification of ToF-SIMS images with surface topography using principal component analysis (PCA) and multivariate curve resolution (MCR). Multivariate analysis simplifies the description of data and is powerful for identifying trends and highlighting chemically significant areas on images. However, many challenges remain with its application to complex images obtained in practical analysis, especially where sample topography or detector saturation[2] gives rise to large non-linear intensity variations in the data. In this study, we use several model samples, including polymer fibres with multi-organic coatings, natural starch grains and human hair, to investigate the merits of different multivariate analysis strategies for samples with topography. The emphasis is placed on the accurate identification and quantification of surface chemistry using careful application of multivariate methods, combined with suitable data selection and preprocessing and valid interpretation of the results. This study extends from our previous work on flat samples[3] and provides helpful guidance in the rapid, unbiased analysis of high-resolution raw spectral data in ToF-SIMS images of increasingly complex multi-organic surfaces and biomaterials.

[1] J L S Lee, I S Gilmore and M P Seah, Appl. Surf. Sci. in press

[2] M R Keenan, V S Smentkowski, J A Ohlhausen and P G Kotula, Surf. Interface Anal. 40 (2008) 97-106

[3] J L S Lee, I S Gilmore and M P Seah, Surf. Interface Anal. 40 (2008) 1-14.

9:40am **AS-WeM6 Methods for Reducing Topographical Influences in ToF-SIMS Spectral Images*, J.A. Ohlhausen*,** *M.R. Keenan*, Sandia National Laboratories

Time-of-Flight Secondary Ion Mass Spectrometry is used to analyze surfaces and surface volumes of many kinds of materials. Many times the surfaces are rough in texture and contain variable materials compositions, thus affecting secondary ion responses. Data interpretation can be influenced unknowingly by topographical differences that might be present. In 3D analysis, data are typically represented as idealized cubes. Actual data will vary from the ideal cube in some unknown way. Spatial distortion from the idealized cube can be caused by several events including starting topography and differential sputtering rates. By understanding morphological and sputtering deviations, a 3D profile can be adjusted to reflect the actual shape of the removed volume. Strategies for measuring topographies and correcting images for 2D and 3D analysis will be presented. Pitfalls and shortcomings will be discussed.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **AS-WeM9 The Effects of Pre-Processing of Secondary Ion Mass Spectrometry (SIMS) Image Data on Self-Modeling Image Analysis*, W. Windig*,** *B.M. Wise*, Eigenvector Research, Inc., *M.R. Keenan*, Sandia National Laboratories

SIMS imaging is a powerful technique for surface analysis. The data from SIMS results in hundreds or thousands of images corresponding to ions of different masses. In order to facilitate data analysis, data reduction techniques are required. One of the tools to reduce the massive amounts of data is self-modeling mixture analysis, which expresses the SIMS image data in a few images representing pure components and their associated mass spectra. This paper will focus on the pure variable approach. A pure variable has contributions from only one component in the mixture data set (i.e. a value of m/e to which only one chemical component contributes) and thus can be used as a relative concentration estimate to resolve the mixture data into pure component spectra and their contributions ("concentrations') in the form of images. Similarly, pure pixels can be selected to resolve the mixture data. Image data are often of a noisy nature. Therefore, pre-processing of the data is often used to improve the results. A popular pre-processing for TOF-SIMS data is based on the Poisson nature of the data. This paper will show a modification of Poisson scaling procedure of the data, which makes it less susceptible to noise. Another way to enhance data analysis is using correlation based techniques to minimize the influence of outlying pixels. This paper will show how the data analysis results, as obtained with the pure variable/pixel approach, can be improved using the proper pre-processing tools, using data sets of actual samples of several chemical mixtures and a fused metal sample.

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.

11:00am **AS-WeM10 Comparison of MAF and PCA for Processing 3-D ToF-SIMS Images of Organic and Biological Samples*, B.J. Tyler*,** University of the West Indies, Trinidad and Tobago

Recent technological advances have facilitated 3-D SIMS imaging of organic and biological samples. To fully realize the potential of this technology, new tools are needed to aid in the image analysis. Even in two-dimensions, obtaining clear contrast between chemically similar regions, distinguishing between chemical and topographical effects and identifying chemical species from a complex ToF-SIMS data set can be a formidable challenge. These challenges become even greater as the size and complexity of the data sets increase due to both the third dimension and the higher useful mass range commonly obtained with cluster ion sources. In the past, we have found that Maximum Autocorrelation Factors (MAF) provides significant improvement over PCA for enhancing image contrast, reducing spectral complexity and facilitating compound identification.[1,2] We have investigated several approaches to generalizing the MAF approach for use in 3 dimensions. These 3-D MAF algorithms have been tested on synthetic images and on a variety of organic and biological 3-D SIMS images. Results have been compared to converntion single-peak data analysis and to PCA results using various scaling options. MAF, which includes information on the nearest neighbors to each pixel, shows clear advantages over PCA, particularly for identifying spase of subtle components in the images. Additionally, MAF is insensitive to pre-processing choices that can dramatically influence PCA results.

[1] Tyler, B.J. Applied Surface Science, Volume 252, Issue 19,30 July 2006, Pages 6875-6882

[2]Tyler, B.J.,Rayal G, Castner D.G., Biomaterials 2007, May 28(15):2412-23.

11:20am **AS-WeM11 SVD + Factor Rotation: A Powerful Alternative to PCA for Spectral Image Analysis*, M.R. Keenan*,** Sandia National Laboratories

Factor analysis has proven an effective approach for distilling high dimensional spectral-image data into a limited number of components that describe the spatial and spectral characteristics of the imaged sample. Principal Component Analysis (PCA) is the most commonly used factor analysis tool; however, PCA constrains both the spectral and abundance factors to be orthogonal, and forces the components to serially maximize the variance that each accounts for. Neither constraint has any basis in physical reality; thus, principal components are abstract and not easily interpreted. The mathematical properties of PCA scores and loadings also differ subtly, which has implications for how they can be used in abstract factor "rotation" procedures such as Varimax. The Singular Value Decomposition (SVD) is a mathematical technique that is frequently used to compute PCA. In this talk, we will argue that SVD itself provides a more flexible framework for spectral image analysis since spatial-domain and spectral-domain singular vectors are treated in a symmetrical fashion. We will also show that applying an abstract rotation in our choice of either the spatial or spectral domain relaxes the orthogonality requirement in the complementary domain. For instance, samples are often approximately orthogonal in a spatial sense, that is, they consist of relatively discrete chemical phases. In such cases, rotating the singular vectors in a way designed to maximize the simplicity of the spatial representation yields physically acceptable and readily interpretable estimates of the pure-component spectra. This talk will demonstrate that this approach can achieve excellent results for difficult-to-analyze data sets obtained by a variety of spectroscopic imaging techniques. 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.

11:40am **AS-WeM12 A Comparison of Multivariate Statistical Analysis Protocols for ToF-SIMS Spectral Images*, V.S. Smentkowski*,** *S.G. Ostrowski*, General Electric Global Research Center, *M.R. Keenan*, Sandia National Laboratories

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) instruments produce raw data sets with a tremendous quantity of data. Multivariate Statistical Analysis (MVSA) tools are being used to boil the massive amount of chemical information into a smaller set of components which are easier to interpret and understand due to species association. Standard Principal Component analysis (PCA) is the most heavily used MVSA algorithm used in the ToF-SIMS community. Other algorithms such as Multivariate Curve Resolution (MCR) have also gained popularity over the past few years. In this work, we compare the as-measured ToF-SIMS spectrum and ion images with four MVSA data analysis protocols; standard PCA, image-rotated PCA, spectra-rotated PCA, and MCR. Image-rotated PCA and spectra-rotated PCA are variations of standard PCA that involve abstract rotation of the principal components, and are designed to enhance either spatial contrast or spectral contrast in the components, respectively. We will show that the four MVSA protocols provide essentially the same information, but accentuate different aspects of the sample's composition and lateral distribution, and that taken together these methods provide a more complete understanding of the sample. We will demonstrate that the component spectra provided by MVSA protocols assists the analyst in understanding species correlation which would have been difficult, if not impossible, using univariate analysis protocols. Since each component image is represented by an associated spectrum (and not just a single peak) enhanced signal-to-noise and contrast is obtained. For the data set described here, MVSA tools identified unexpected species, which were not obvious in the as measured data.

## 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 use to perform local nanoscale assays on the cell surface so as to perform single channel recording[5] 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 level[3] and this is being used to probe the structure of the cell membrane using single molecule fluorescence tracking.

References

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[2]. PNAS 104,17662-17667 (2007)

[3]. Phys. Chem. Chem. Phys. 7 , 2859-2866 (2005)

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[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 gatability 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. Pirollo, 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. Pirollo, 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.

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[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 ß-galactosidase molecules that can be attributed to different enzyme conformations. When a slow-binding inhibitor was added to single ß-galactosidase molecules inhibited and active states of ß-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 ß-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-assembles 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.

8:40am **BO+AS+BI+NC-WeM3 Polymer Brushes: Patterns, Architecture and Functionality**, ***K. Carter***, University of Massachusetts **INVITED**

We embed chemical functionality into crosslinked network polymers. This functionality can be accessed in subsequent reactions, allowing for the creation of surfaces with controlled size and chemistry. We have demonstrated that this methodology works from flat films, patterned nanostructures and particles, providing a powerful, robust, new technique for functionalizing surfaces. We have been exploring polymer interfaces of the polymer networks and subsequent modification of the network surface functionality. We add a functional comonomer to our curable polymer resin and after molding a fraction of this incorporated functionality is present at the surface of the polymer and available for subsequent reactions. This concept of embedded functionality has been exploited in a number of ways. For example, we have used these surfaces for selective the metallization and we have been exploiting the surface functionality to accommodate the attachment of semiconducting polymers and bioactive materials. The synthesis, characterization and use of these new materials and related techniques are discussed.

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 Tunnelling 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.

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

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 etero-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 Merve 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 Hyperthemal 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.

## Electronic Materials and Processing
## Room: 210 - Session EM-WeM

## High-K Oxides and High Mobility Substrates
## Moderator: R.M. Wallace, University of Texas at Dallas

8:00am **EM-WeM1 Spectroscopic Detection of Conduction Band Edge Defects in $HfO_2$, Hf Si Oxynitride and Stacked Hf Si Oxynitride/$HfO_2$ High-k Dielectrics: Extraction of Defect States from O K Edge NEXAS Spectra**, *K.B. Chung, H. Seo, J.P. Long,* ***G. Lucovsky***, North Carolina State University

A novel approach for eliminating Ge-N bonding at Ge-high-k dielectric interfaces from sacrificial Ge nitride interfacial transition regions (ITRs) used to passivate the Ge substrate against oxidation during film deposition. The GeN ITRs can be effectively eliminated during an 800°C post-deposition one minute anneal in Ar leaving the $HfO_2$ films in direct bonding contact with Ge(100) or Ge(111) substrates. This paper presents a study of band edge electronic structure, including band edge defects as function of annealing temperature by comparing near edge X-ray absorption spectra (NEXAS), O $K_1$ and N $K_1$ edges, for films deposited on a ~0.6-0.8 nm interfacial Ge-N layer, and after partial and complete removal of interfacial Ge-N and/or Ge-O bonding for anneals up to 800°C in Ar. Three types of dielectrics have been addressed: i) $HfO_2$, ii) high $Si_3N_4$ content Hf Si oxynitride alloys, and iii) stacked dielectrics comprised of high $Si_3N_4$ content Hf Si oxynitride alloy/$HfO_2$. One of the primary sources of defects in the $HfO_2$ films is associated with the incorporation of Ge, which has been detected in SXPS/UPS spectra. Finally defects identified in $HfO_2$ spectroscopically, explain large differences in the tunneling currents.

8:20am **EM-WeM2 ARXPS Study of the Early Stages of the Formation of the $HfO_2$/Si and $HfO_2$/$SiO_2$ Interfaces**, *M.D. Morales-Acosta,* ***A. Herrera-Gomez***, Cinvestav-Unidad Queretaro, Mexico, *F.S. Aguirre-Tostado, J. Kim, R.M. Wallace*, The University of Texas at Dallas

The interfacial layer that is formed as hafnium oxide is deposited on silicon affects the performance of hafnium-based C-MOS devices. Although the composition of the interfacial layer could be evaluated from electrical measurements,[1] a more direct approach is desirable. The ideal technique for this type of studies is ARXPS because of its unparallel chemical and depth resolution. We performed high resolution ARXPS studies on ALD HfO2 film grown on H-terminated and 1nm SiO2-terminated Si(001) surfaces employing 5 and 30 cycles (H2O and TEMA-Hf). The deconvolution of the peaks was done robustly. Since surface potentials could also cause “chemical” shifts on the binding energies, the physical origin of the different peaks was assigned not only from the peak position but also from the detailed analysis of the take-off angle dependence of the peak area. It was possible to learn about the early stages of the HfO2/SiO2 interface formation since the thickness of the hafnium oxide layer for the samples with 5 ALD cycles were less than one monolayer. Although the 30 cycle ALD growth resulted in stoichiometric 2nm HfO2 films for both surfaces, in the early stages the growth of the HfO2 was more efficient for the SiO2-terminated sample. The first ALD cycles in the H-terminated samples caused the formation of 1.5ML of oxidized silicon. The Si 2p binding energy was 102.9eV, 0.4eV smaller than for the SiO2-terminated samples. Our analysis shows that this difference could be associated to the known dependence of the Si 2p binding energy on the oxide growing process, and not to the formation of a hafnium silicate layer for the H-terminated surfaces. As reported elsewhere,[2] there is a component (Hf*) with Hf 4f binding energy 0.6eV higher than for hafnium oxide. The analysis strongly suggests that Hf* could be associated to the first layer of HfO2 in contact with the SiO2, and not to a hafnium silicate layer. We concluded that the ALD process produced an abrupt SiO2/HfO2 interface, even for the H-terminated samples. A clear description of the self-consistent ARXPS analysis will be presented. This work was supported by the Semiconductor Research Corporation and the Texas Enterprise Fund.

[1] S. K. Dey, A. Das, M. Tsai, D. Gu, M. Floyd, R. W. Carpenter, H. De Waard, C. Werkhoven, and S. Marcus. J. Appl. Phys. 95, p. 5042 (2004).

[2] N. Barrett, O. Renault, J.F. Damlencourt, and F. Martin. J. Appl. Phys. 96, p. 6362 (2004).

8:40am **EM-WeM3 Characterization of High-k Dielectric and Metal Gate Film Stack by AR-XPS**, ***G. Conti***, *Y. Uritsky, C. Lazik, S. Hung, N. Yoshida, M. Agustin, X. Tang, R. Wang*, Applied Materials Inc.

The implementation of a higher-k hafnium-based dielectric coupled with an atomically engineered oxynitride interface addresses gate leakage while maintaining high mobility. In conjunction with the new dielectric stack, metal gates are replacing polysilicon gate electrodes for material compatibility and performance. Devices made with high-k/metal gates can achieve >100x improvement in gate leakage, with significantly greater switching speed. The desirable properties of the dielectric High-K layer are

: high dielectric constant; low leakage current; and thermal stability against reaction or diffusion to ensure sharp interfaces with both the substrate Si and the gate metal . Extensive characterization of such materials in thin-film form is crucial not only for the selection of alternative gate dielectrics and processes, but also for the development of an appropriate metrology of the high-k films on Si. This paper will report recent results on structural and compositional properties of Al2O3 deposited on 20A ALD HfO2 / 8A SiO2 . This stack was capped with 20A TiN . Angle-resolved XPS showed that after the high temperature anneal Al diffused into the dielectric stack with its concentration peaking at the HfO2/SiO2 interface and some remaining at the HfO2 surface. No Al was detected near the Si substrate interface suggesting that the insertion of Al2O3 cap layer at the high-k/metal gate interface and subsequent high temperature process should not degrade the device channel mobility. The AR-XPS and the TEM results are compared to the electrical data.

9:00am **EM-WeM4 Density-Functional Theory Molecular Dynamics Simulations of a-Al$_2$O$_3$/Ge(100)(2x1), a-Al$_2$O$_3$/In$_{0.5}$Ga$_{0.5}$As, a-Al$_2$O$_3$/In$_{0.5}$Al$_{0.5}$As/In$_{0.5}$Ga$_{0.5}$As**, *E. Chagarov, **A.C. Kummel***, University of California, San Diego

Amorphous oxide-semiconductor interfaces are keys to the performance of all metal-oxide field effect transistors (MOSFETs), but little is known about the exact bonding geometry at the interface. In this study, the bonding of a single amorphous oxide onto three semiconductors is compared to understand selective bond formation and intermixing since interfaces with non-polar bonds, no intermixing, and no half-filled dangling bonds are optimal for MOSFET devices. The local atomic and electronic structure of a-Al$_2$O$_3$/Ge(100)(2x1), a-Al$_2$O$_3$/In$_{0.5}$Ga$_{0.5}$As, and a-Al$_2$O$_3$/In$_{0.5}$Al$_{0.5}$As/In$_{0.5}$Ga$_{0.5}$As interfaces were investigated by density-functional theory (DFT) molecular dynamics (MD) simulations. Realistic amorphous a-Al$_2$O$_3$ samples were generated using a hybrid approach including classical and DFT molecular dynamics. Each amorphous oxide/semiconductor interface was formed by placing an amorphous oxide sample on a slab of one of the semiconductors and annealing the stack at 700K / 800K and 1100K; subsequently, the stack was cooled and relaxed to get the final oxide-semiconductor interfacial bonding structure. The a-Al$_2$O$_3$/Ge interface demonstrates strong chemical selectivity with Al atoms migrating out of interface into the oxide bulk and O atoms migrating into the interface region resulting in interface bonding exclusively through Al-O-Ge bonds creating a large interface dipole; this exclusive Al-O-Ge bonding is due to Al-O bonds being more energetically favorable than Al-G bonds. During annealing of a-Al$_2$O$_3$/In$_{0.5}$Al$_{0.5}$As/In$_{0.5}$Ga$_{0.5}$As, Al migrates from InAlAs to a-Al$_2$O$_3$, demonstrating interfacial mixing; the intermixing is driven by the high energy of formation for Al-O bonds. The a-Al$_2$O$_3$/In$_{0.5}$Ga$_{0.5}$As interface has polar As-Al bonds and In/Ga-O bonds of opposite dipole direction, low lattice distortion, and no intermixing. The formation of two types of bonds with opposite dipoles is driven by electronegativity: Al, an electron donor, bonds to As an electron acceptor while O, an electron acceptor bonds to In/Ga, electron donor.

9:20am **EM-WeM5 Atomic Layer Deposition (ALD) of Amorphous High-k Dielectric Films of La$_{(1-x)}$M$_x$O$_{3/2}$, M = Al, Sc, Lu, Y and La**, ***H. Wang**, M. Coulter, Y. Liu, J.J. Wang, R.G. Gordon,* Harvard University*, J.S. Lehn, H. Li, D.V. Shenai*, Rohm and Haas Electronic Materials

ALD was used to deposit films containing lanthanum and other trivalent elements aluminum, scandium, lutetium and yttrium. The precursors are N,N'-dialkylformamidinates or acetamidinates, except for aluminum, for which trimethylaluminum was used. The oxygen source was water vapor, which was sometimes supplemented with molecular oxygen to eliminate oxygen vacancies. Substrates used include silicon, germanium, gallium arsenide, ruthenium and titanium nitride. The films are amorphous as deposited, and have no interfacial layer between the dielectric an silicon. The films remain amorphous after rapid thermal annealing to temperatures as high as 1000 $^{o}$C. High dielectric constants and very low leakage currents were measured. Dielectric constants remain the same even when the film thickness is reduced to ~ 5 nm, leading to EOT values < 1 nm with leakage currents < $10^{-3}$ A cm$^{-2}$.

10:40am **EM-WeM9 Electrical and Physical Properties of High-k Gate Dielectrics on III-V Semiconductors**, ***E.M. Vogel**, C.L. Hinkle, A. Sonnet, F.S. Aguirre-Tostado, M. Milojevic, K.J. Choi, H.C. Kim, J.G. Wang, H.C. Floresca, J. Kim, M.J. Kim, R.M. Wallace*, The University of Texas at Dallas **INVITED**

Because of a significantly higher electron mobility compared to silicon, III-V semiconductors (e.g. GaAs, InGaAs) with high-k gate dielectrics (e.g. Al$_2$O$_3$, HfO$_2$) are being considered for future Metal Oxide Semiconductor Field Effect Transistors (MOSFETs). However, device performance has been limited by high electrically active interfacial defect density. Various physical characterization techniques including monochromatic x-ray photoelectron spectroscopy (XPS) and high-resolution transmission electron microscopy (HRTEM) are used to study the physical properties of atomic-layer-deposited Al$_2$O$_3$ and HfO$_2$ dielectrics with various interlayers (e.g. silicon), precursors and surface treatments. Characterization and modeling of the electrical properties of MOS capacitors and MOSFETs is correlated to the details of the bonding arrangements and physical properties of the dielectric stacks. The results suggest that proper selection of interlayer, ALD precursors, and surface treatment can result in selective interfacial bonding arrangements and associated device electrical properties.

11:20am **EM-WeM11 Surface Structure and Fermi Level Determination of Oxides/III-V Interface**, ***J. Shen**, A.C. Kummel*, University of California, San Diego

We have used scanning tunneling microscopy (STM) and density functional theory (DFT) calculations to both identify the group III rich III-V surface reconstruction and to identify the bonding structure for oxide on these surfaces. In-rich InAs(001)-(4×2) can readily be prepared by decapping of As2 capped InAs(001) wafers. STM results reveal that In-rich InAs(001)-(4×2) has a very different atomic structure than Ga-rich GaAs(001)-ζ(4×2) structure even though the surfaces have similar symmetry. The InAs(001)-(4×2) is denoted as the β3(4×2) and has a unit cell consisting of two undimerized group III atoms on the row and two group III dimers in the trough. STM results showed that the initial deposited In2O molecules bond to the edges of the rows and most likely form new In-As bonds to the surface without any disruption of the clean surface structure. Annealing the In2O/InAs(001)-(4×2) surface at 400˚C results in formation of flat order monolayer rectangular islands onto which oxide grows in a layer-by-layer mechanisms with amorphous structure. In0.53Ga0.47As is a good candidate for a III-V MOSFET due to its high carrier mobility, low density of thermal carriers, and ability to be grown lattice matched on semi-insulator InP substrates. STM images of the clean surface indicate that the In0.53Ga0.47As(001)-(4×2) surface reconstruction is similar to the InAs(001)-(4×2) structure. The DFT calculations reveal that the some of the trough dimers are buckled, which is consistent with the STM images showing that the trough has poor order. Ga2O was deposited on the surface to determine how oxide adsorbates bond to In0.53Ga0.47As(001)-(4×2) clean surface. The bonding structure of the annealed Ga2O/In0.53Ga0.47As(001)-(4×2) is similar to that of In2O/InAs(001)-(4×2); however, the Ga2O/ In0.53Ga0.47As(001)-(4×2) islands are more weakly ordered than the In2O/InAs(001)-(4×2) islands. For both In2O/InAs(001)-(4×2) islands and Ga2O/ In0.53Ga0.47As(001)-(4×2), the oxide adsorbates never cause the abstraction of any surface atoms on the InAs and In0.53Ga0.47As(001)-(4×2) surfaces; furthermore, for monolayer oxide films, the oxide molecules only occupied specific sites. After high temperature annealing, the oxide desorbs from the surface and the clean (4×2) surface is restored. This is consistent with the formation of a smooth interface between the oxide and the semiconductor.

11:40am **EM-WeM12 High-K Dielectrics/High Mobility Channel Interface Optimization for Future CMOS Technology**, ***L. Yu**, T. Feng, Q. Jiang, H.D. Lee, C.L. Hsueh, A.S. Wan, D.D.T. Mastrogiovanni, Y. Xu, T. Gustafsson, E. Garfunkel*, Rutgers, The State University of New Jersey

High-k dielectrics have been adapted as gate oxide in order to prolong the Moore's law of CMOS transistor scaling to a critical length of 45 nm and beyond. Also, replacing Si with a higher mobility material (for example, Ge and III-Vs) as transistor channel is expected to further enhance the transistor performance. Thus, the idea of combining those two advances in one process has attracted many research efforts from both academia and industry. However, the task has been difficult due to the lack of proper treatment to the oxide/channel interface. The defect states at the interface or inside dielectrics can enhance carrier scattering and degrade device threshold voltage. Further more, the chemical instability and compatibility at the interface are often detrimental to device performance. Several studies, including ours, showed that chemical cleaning and subsequent passivation (for example, with ammonium sulfide) prior to dielectrics deposition on both Ge and GaAs channels can greatly reduce the interface state density (Dit). We have established tools that enable ALD and sputtering deposition of the CMOS gate stacks along with in.situ. characterization by MEIS (Medium Energy Ion Scattering) and XPS. It allows us to determine, with high spatial resolution, the composition, structure and thermal stability of gate stacks on various channels. We will present the in. situ. characterization results of Al2O3 and HfO2 based gate stacks on chemically treated Ge and GaAs surface. These results will be directly correlated with studies of gate stack electrical properties and electronic structure.

## 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. Whitney*, 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 ($BO_xN_{1-x}$) thin films to fabricate capacitors for high temperature applications. Deposited $BO_xN_{1-x}$ 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. $BO_xN_{1-x}$ 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 ($BO_xN_{1-x}$) 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 (α = 0°) are continuous, and approximately replicate the rough surface morphology of the underlying GDL. In contrast, glancing angle deposition (GLAD) with α = 85° and continuously rotating substrates yields highly porous layers consisting of vertical Pt nanorods. At 0.40 mg/cm$^2$ 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/cm$^2$ 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/cm$^2$, respectively) show 1.7 and 0.8 A/mg. In contrast, at low current density of 0.10 A/cm$^2$, the continuous layers (0.70 V with 0.25 mg/cm$^2$ Pt) outperform GLAD cells even with relatively high Pt loadings (0.65 V with 0.40 mg/cm$^2$ 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.

## In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
## Room: 310 - Session IS+SY+SS-WeM

## In Situ Spectroscopy – Interfacial Science and Catalysis
**Moderator:** D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SY+SS-WeM1 Probing the Electrochemistry of Ceria in Solid-Oxide Fuel Cell Anodes under Operation using Ambient-Pressure XPS**, ***H. Bluhm***, *J.T. Newberg, Z. Liu, Z. Hussain,* Lawrence Berkeley National Laboratory, *S.C. DeCaluwe, C. Zhang, G.S. Jackson,* University of Maryland, College Park, *F. El Gabaly, R.L. Farrow, K.F. McCarty, M.A. Linne, A.H. McDaniel*, Sandia National Laboratories

Solid-oxide fuel cells (SOFCs) are an important technology for converting chemical energy to electrical energy. A compelling advantage of SOFCs is the ability to utilize fuels such as hydrogen, synthesis gas, and hydrocarbons. In a conventional SOFC, selective catalytic and charge transfer processes produce $O^{2-}$ ions at the cathode/electrolyte interface, which then diffuse through a dense electrolyte to an anode/electrolyte interface where adsorbed fuel species are oxidized. Ceria ($CeO_2$), a mixed conductor capable of transporting both $O^{2-}$ ions and electrons, is being considered as a coke-resistant anode catalyst to improve SOFC performance. A key unknown about ceria-catalyzed anodes is the cerium (Ce) oxidation state during fuel cell operation. Cell performance is critically affected by the Ce oxidation state because $Ce^{3+}$ and $Ce^{4+}$ states coexist in $CeO_2$, and both electronic and ionic conductivities are determined by the abundance of $Ce^{3+}$. To exploit the potential of ambient-pressure XPS to characterize functioning electrochemical devices, we have fielded an SOFC experiment on beamline 11.0.2 at the Advanced Light Source. A single chamber cell was created by patterning working and counter electrodes from ceria and platinum atop single crystal yttria-stabilized zirconia (YSZ) electrolyte. The cell was characterized in atmospheres of $H_2/H_2O$ and $H_2/O_2/H_2O$ under forward and reverse polarization at approximately 973 K and 0.5 Torr. Standard chronoamperometric and impedance measurements were conducted simultaneously with ambient-pressure XPS. A focused x-ray beam (diameter < 0.1 mm) was used to spatially resolve changes in the Ce oxidation state as a function of position between counter and working electrodes under positive and negative bias. Electrochemically induced changes in the Ce oxidation state were directly observed and were dependent upon electrode polarization and proximity to electrochemically active regions. In addition, the oxidation state and surface potential of the YSZ electrolyte were also characterized. Implications of our findings on understanding the electrochemical mechanisms of SOFC operation with ceria anodes will be discussed.

This research was supported by the U. S. Department of Energy under Contract No.DE-AC04-94AL85000 (Sandia) and DE-AC02-05CH11231 (LBNL). UMD participants were supported by the Office of Naval Research under Contract No: N000140510711.

8:20am **IS+SY+SS-WeM2 In-situ Dynamics of CO Oxidation on Pt(110) with Ambient Pressure XPS**, *Z. Yang, F. Aksoy, Z. Liu,* Lawrence Berkeley National Laboratory, *H. Kondoh,* Keio University, Japan, *P. Ross,* Lawrence Berkeley National Laboratory, ***B. Mun***, Hanyang University, Korea

Considering the recent increasing demands of improved catalytic materials in energy industry, the understanding clear mechanism of catalytic reactions at an atomic scale level has become more critical. Especially, the formations of oxide on transition metal surface have been actively studied due to its importance in fundamental understanding of heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxide on Pt [110] received much attention due to its unique surface reconstruction under high pressure reaction conditions. Previously, with the combinations of high pressure STM and in-situ x-ray diffraction, the formation of surface Pt oxide is observed when the reaction rate is enhanced, and showed the surface oxide formed is stable with carbonate species.[1,2] In this work, using the ambient pressure XPS (AP XPS) and mass spectrometer, the in-situ dynamics of CO oxidation on Pt [110] surface are discussed under close to the realistic condition. Under the reaction conditions (T=420K) with the pressure of CO and O gases at 450 mTorr in the AP XPS chamber, our results show that a) the chemisorbed oxygen is not stable under the reaction conditions, b) there is no formation of surface oxide on Pt surface under our reaction conditions.

[1] B.L.M. Hendrikson and J.W.M. Frenken, Phys.Rev. Lett. 89, 046101(2002)

[2] M.D. Ackermann et al.,Phys.Rev. Lett. 95, 255505(2005).

8:40am **IS+SY+SS-WeM3 Medard W. Welch Award Lecture: Novel X-ray Photoelectron Spectroscopy Techniques for In Situ Studies of Surfaces in Equilibrium with Gases in the Torr Pressure Regime: Application to Catalysis and Environmental Sciences**, ***M. Salmeron****, Lawrence Berkeley National Laboratory **INVITED**

X-ray photoelectron spectroscopy (XPS) ideally suited to investigate the chemical nature of surfaces. Due to the scattering of eletrons by gas molecules XPS is in generally performed under high vacuum conditions. However, because of thermodynamic and/or kinetic limitations, the surface chemical state observed under vacuum is not necessarily the one under the pressures that are relevant to catalysis and the environment (Torr to atmosphere). We developed a electrostatic lens system combined with differentially-pumped chambers that permits operation at pressures of up to 10 Torr. I will describe this ambient pressure XPS apparatus and show recent applications to studies of oxidation and heterogeneous catalytic reactions. I will also show how the technique can solve and advance our fundamental knowledge of surfaces in environmental science studies, particularly in the presence of water vapor.

9:20am **IS+SY+SS-WeM5 Nano Scale X-ray Absorption Spectroscopy of In Situ Modified Samples using Scanning Transmission X-ray Microscope**, ***T. Tyliszczak***, Lawrence Berkeley National Laboratory **INVITED**

Observation and spectroscopy of in situ chemical reactions on nanoscale is important but not easy task. It is important in many fields, especially in research of heterogeneous catalysts. Typically, transmission electron microscopy has been used under in situ conditions, but the strict low pressure requirements for this technique prevent it from being carried out under catalytically relevant conditions. Recently however, by using a specially designed microreactor, promising TEM experiments have been performed under 1 bar conditions but with a limitation of gases which could be used.[1] Other techniques include STM, fluorescence and optical microscopy. Most of these techniques allow imaging of intermediate steps of reactions with limited information about reaction chemistry. Scanning Transmission X-ray Microscopy (STXM) with relatively good spatial resolution of 20-30 nm, high chemical sensitivity and much lower restriction on the environment of a sample is promising to provide new insides into the catalytic reactions. By using soft X-rays (130 -2000 eV) as a microprobe, it is possible to study both the active phase of the catalyst, through absorption edges of the inorganic species, and the organic, reactant phase of the catalyst through the absorption edges of carbon, oxygen and nitrogen. While the maximum spatial resolution of STXM is still significantly worse than for example STEM-EELS, there are important advantages in application STXM, most notably the superior spectral resolution and the reduced radiation damage in the study of softer core hole edges (C, N, O K-edges) and hydrated samples. Bell et al.[2] first demonstrated the use of STXM for the study of a catalytic material under in situ conditions. Their cell design allowed sample treatments in gases up to 260 °C. E. de Smit et al.[3] used modified ETEM cell to in situ studies of a complex iron oxide based Fischer-Tropsch catalyst. They were able to heat the sample up to 500oC at gas pressure up to 1.2 bar opening a way to study

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* Medard W. Welch Award Winner

real catalyst normal conditions. The cell, manufactured as a microelectromechanical system (MEMS), basically consists of a 500 * 500 mm reactor chamber connected by micrometer-sized gas-flow channels. Two amorphous Si3N4 optical windows, etched down to a thickness of 10 nm in certain places, separate the reactor from the outside environment. The thickness of the reactor, thus gas path length, is only about 50 mm, and therefore ensures minimum attenuation of the X-ray light by the gas phase molecules. Spacers, placed between the windows prevent the windows from sticking together. The sample is loaded by flowing a powder suspended in a solvent (e.g. ethanol) through the reactor and subsequent drying. After drying, the sample is supported on the SiNx windows. E. de Smit et al were able to track reaction steps measuring changes in chemical state of iron and oxigen. They also investigated a role of carbon in the reaction. Progress in technical development of reaction cell and increasing resolution of the x-ray microscope provide opportunity to investigate gas - solids or liquid - solids in situ, in relevant conditions on nanometer scale.

[1] J. F. Creemer, S. Helveg, G. H. Hoveling, S. Ullmann, A. M. Molenbroek, P. M. Sarro and H. W. Zandbergen, Ultramicroscopy, In Press, Accepted Manuscript.

[2] I. J. Drake, T. C. N. Liu, M. Gilles, T. Tyliszczak, A. L. D. Kilcoyne, D. K. Shuh, R. A. Mathies and A. T. Bell, Review of Scientific Instruments, 2004, 75, 3242-3247.

[3] E. de Smit , I. Swart, J. F. Creemer , G. H. Hoveling, M. K. Gilles , T. Tyliszczak, C. Morina, P. J. Kooyman, H. W. Zandbergen, B. M. Weckhuysen and Frank M.F. de Groot, Nature, submitted manuscript.

10:40am **IS+SY+SS-WeM9 In Situ Synchrotron X-ray Study of the Synthetic Processes for Inorganic Solid Oxide Nanomaterials**, *Y. Mao*, ***J. Dorman***, *J.P. Chang*, University of California at Los Angeles

Nanostructured crystalline inorganic solid oxides show various intriguing properties and process many important technological applications. To better control the property and device performance of materials, growth kinetic and mechanistic information of structure changes should be pursued to provide feedback for the development of new "designer" materials to meet the challenges of the future. Time-resolved in situ experimentation represents the most likely means, especially with the synchrotron radiation as the x-ray source due to its high energy flux. In this study, we focus on advanced luminescent nanomaterials, since they have practical applications in nearly all devices involving the artificial production of light and are applicable in nanoscaled electronics, photonics, display and advanced bioanalysis. In this talk, we present our recent investigation by in-situ time-resolved synchrotron x-ray diffraction (XRD) and absorption spectroscopy (XAS) on the synthesis of rare-earth doped metal oxide nanostructures, including Er:$Y_2O_3$ nanotubes and nanoparticles and Er: $La_2(Zr_xHf_{1-x})_2O_7$ nanoparticles, by hydrothermal and molten-salt syntheses.[1,2,3] Our results demonstrate that in situ XRD and XAS data support each other. For the hydrothermal synthesis of Er:$Y(OH)_3$ nanotubes, the hydroxide phase starts to form immediately and continues to grow. For the dehydration process from Er:$Y(OH)_3$ nanotubes to Er:$Y_2O_3$ nanotubes, the dehydration starts at ~250°C and completes at 450°C and an intermediate oxyhydroxide phase was found for the first time. Furthermore, the in situ XRD study provided guidance on the selection of proper annealing temperature for the molten salt synthesis of Er:$Y_2O_3$ and Er: $La_2(Zr_xHf_{1-x})_2O_7$ nanoparticles. Their growth kinetics will be obtained from further investigation of these processes under different ramp rates and reaction temperatures.

[1] Mao, et al. Synthesis and luminescence properties of erbium-doped $Y_2O_3$ 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. $La_2Zr_2O_7$ and $La_2Hf_2O_7$ nanoparticles from single-source complex precursors: kinetically modified synthesis and luminescent properties, submitted (2008).

11:00am **IS+SY+SS-WeM10 Surface Chemistry of Model Solid Oxide Fuel Cells Studied In-Situ by Synchrotron Based Photoemission Microscopy and Spectroscopy**, ***K. Adib***, *M. Backhaus-Ricoult*, *T.P. St. Clair*, Corning Incorporated, *B. Luerssen*, Justus Liebig Universitaet, Germany, *L. Gregoratti*, *A. Barinov*, Sincrotrone Elettra, Italy

We have used synchrotron based X-ray photoemission spectroscopy (XPS) and scanning photoemission microscopy (SPEM) to study the surface compositions of model solid oxide fuel cells containing $La_xSr_{1-x}MnO_3$ (LSM) cathode and yttrium-stabilized zirconia (YSZ) electrolyte under various oxygen pumping conditions at approximately 650°C and an oxygen partial pressure of $5x10^{-7}$ mbar. SPEM in the vicinity of the LSM/YSZ interface indicates depletion of Mn atoms from the LSM surface and their accumulation on the YSZ surface with increasing cathodic bias. XPS indicates that the accumulation of Mn on the YSZ is accompanied by reduction in the oxidation state of Mn. Within a wide range of applied voltage these changes are reversible. XPS of oxygen core levels also indicates that under cathodic bias, during which oxygen is incorporated from the surrounding gas into the cathode and pumped through the electrolyte, an additional oxygen species is present on the surface of LSM. The concentration of this species increases with increasing cathodic bias and we tentatively assign this species to surface oxygen as distinct from lattice oxygen. On the YSZ surface, no such change in the concentration of the surface oxides with cathodic bias was detected emphasizing the role of LSM in enhanced adsorption of oxygen.

11:20am **IS+SY+SS-WeM11 Organic Solar Cells and Microgels: Examples of In Situ Applications of Soft X-ray Microscopy**, ***H. Ade***, North Carolina State University **INVITED**

Soft x-ray microscopy has achieved a spatial resolution of ~ 30-40 nm. At the same time, soft x-rays are penetrating enough to investigate samples sandwiched between thin silicon nitride membranes or thin metal layers. This allows the investigation of wet samples or samples sandwiched between thin electrodes. When coupled with Near Edge X-ray absorption Fine Structure (NEXAFS) spectroscopy, unique characterization capabilities results that range from compositional mapping, to charge state determination and induced current measurements. This presentation will review the state-of-the-art of NEXAFS microscopy. The focus will be on a range of in-situ applications and most extensively on the characterization of microgels and organic solar 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 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/$Cu_3Au$(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

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* Falicov Student Award Finalist

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] Dvakonov, 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, $BaFe_{12}O_{19}$) 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 ($<1\times10^{-5}$ Torr) and solid source Ba and Fe effusion cells at substrate temperature ranging from 300~800ºC. High quality film with strong c-axis aligned normal to the substrate and low coercivity (200 Oe) was achieved at 750 ºC and $2\times10^{-6}$ 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 $2 \times 2$ $\mu m^2$) 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 $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ 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 $La_{5/8-x}Pr_xCa_{3/8}MnO_3$ (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 Anisotopy in Epitaxial FePt(100) Films**, ***Z. Lu*****, *M.J. Walock, P. LeClair, W.H. Bulter, 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 $K_u=7x10^7$ erg/cm$^3$. 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 $Fe_{50}Pt_{50}$ 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 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 $Gd_2O_3$ Nanoparticles to be used for MRI Contrast Enhancement**, *M. Ahren, L. Selegard, N. Abrikossova, 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 Photoelcetron 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

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* Falicov Student Award Finalist

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 $SiO_2$[1] 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 graphene[3] limits the room-temperature mobility to 200,000 $cm^2$/Vs at a carrier density of $10^{12}$ $cm^{-2}$, higher than any known material. However, conduction in current graphene samples is limited almost entirely by extrinsic scattering due to charged impurities in the substrate[2] and substrate polar optical phonons[3] 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 $SiO_2$,” 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 $SiO_2$,” 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).

## 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

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* Peter Mark Memorial Award Winner

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 $CH_3$ 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 $C^{2+}$ 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 from In, Ga, and Al[1] 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 QPlus[1] 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 heterostuctured 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 data[1] 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 QD[4] is also taken into account in this study. We compare our results with those obtained by kp-calculations[5] 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.

## Plasma Science and Technology
## Room: 304 - Session PS1-WeM

### Plasma-Surface Interactions in Materials Processing I

**Moderator:** S. Agarwal, Colorado School of Mines, L. Stafford, Universite de Montreal, Canada

8:00am **PS1-WeM1 Studying the Interaction of Atomic Hydrogen with a-Si:H Thin Films using Evanescent-Wave Cavity Ring-Down Spectroscopy**, *F.J.J. Peeters, J. Zheng, I.M.P. Aarts, A.C.R. Pipino, W.M.M. Kessels,* ***M.C.M. van de Sanden***, Eindhoven University of Technology, The Netherlands

Near-IR Evanescent-Wave Cavity Ring-Down Spectroscopy (EW-CRDS) is applied to an a-Si:H thin film subjected to quantified H fluxes from an atomic H source in the range of $(0.4\text{-}2)\text{x}10^{14}\text{cm}^{-2}\text{s}^{-1}$. To this end a ~40 nm a-Si:H film was grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by thermal decomposition of silane on a hot filament. The observed changes in the optical loss during H dosing are attributed to the creation and healing of sub-gap Dangling Bond (DB) defect states and were measured with a sensitivity of $\sim 10^{-6}$ and a time resolution of 33 ms. The DB density is shown to increase during H dosing cycles and the DBs reversibly 'heal' when the H flux is terminated. The effect increases in magnitude with H flux and approaches saturation at the highest attainable flux of $2\text{x}10^{14}$ $\text{cm}^{-2}\text{s}^{-1}$. Initial rates for both uptake and healing are linear with flux. Through the use of polarizing optics the CRDS signal was split into s- and p-polarized components, which, combined with field calculations, revealed that H-induced DB formation is not limited to the surface of the film but progresses into the bulk with a penetration depth of ~10 nm. The steady-state penetration depth appears to be independent of flux within the range of our experiment. A similar process is observed for defect creation during growth of the film. Extensive kinetic modeling of the observed behavior is used to understand the hydrogen-material interactions and DB formation in a-Si, which are of key importance in a-Si:H thin film solar cells.

8:20am **PS1-WeM2 Unraveling the Importance of the Bimodal Energy Distribution of Bombarding Ions in Fluorocarbon Plasma Etching**, ***F.L. Buzzi***, *Y.H. Ting, A.E. Wendt*, University of Wisconsin-Madison

Ion bombardment provides a key benefit in plasma etching for microelectronics fabrication and other materials processing applications. A sheath electric field accelerates ions into the substrate so they strike at normal incidence, contributing energetic and reactive species to enable anisotropic etch profiles. The energy of the bombarding ions is a significant parameter, and is typically controlled coarsely by adjusting the time-averaged sheath voltage through the application of a sinusoidal bias voltage to the substrate electrode. The sinusoidal voltage waveform produces a broad "bimodal" ion energy distribution (IED) at the substrate, with two ion flux maxima, at respective energies considerably above and below the average. In order to deconvolve the effect of ions of multiple energies bombarding the substrate simultaneously, we have manipulated the waveform of the bias voltage to produce two ion flux maxima. By systematically tailoring the shape of the waveform, the energies and relative fluxes of the two IED peaks are varied independently over a 100 to 500 eV range in a fluorocarbon-based helicon plasma, while silicon dioxide and photoresist etch rates are monitored. Fluorocarbon plasmas create a competition between deposition and etching on the substrate surface, so that with a single IED peak at 100 eV, net deposition is observed, while etching with a monotonically increasing etch rate is observed for a single peak in the 200 to 500 eV range. Two experiments were conducted in which a 100 eV IED peak was combined with a higher energy peak, varying the energy and relative flux of the high energy peak, respectively. In both cases, a relatively small contribution of high energy ions clearly leads to considerable etch rate enhancement, higher than predicted by a linear combination of single peak etch rates at the two energies. We attribute this to the effect of high energy ion bombardment on the chemical composition at the substrate surface, altering the competition between etching and deposition. When net deposition is suppressed, 100 eV ions will interact with the underlying substrate to more effectively enhance etching. The etch rate data provide evidence that for the process examined, a high energy group of ions, comprising as little as 25% of the total flux. produces this suppression, enabling lower energy ions to contribute to etching reactions. These results highlight the significance of the shape of the IED on plasma process outcomes.

### 8:40am **PS1-WeM3 Diamonds and New Carbon Allotropes from Carbon Nanotubes at Room Temperature**

***M.J. Behr********, University of Minnesota, *A.R. Muniz, T. Singh, D. Maroudas,* University of Massachusetts, Amherst, *E.S. Aydil*, University of Minnesota

Interactions of reactive plasmas with nanostructured materials enable the synthesis of materials that would not be expected to form at low temperature and in vacuum. As a remarkable example, in this presentation, we report the plasma synthesis of diamonds and other new carbon allotropes from multiwalled carbon nanotubes (MWCNTs) at room temperature. We exposed MWCNTs to hydrogen atoms created by plasma dissociation of dihydrogen gas in a downstream inductively coupled plasma and observed the transformation of the nanotubes to various crystalline carbon structures, even at room temperature. Examination of the H-exposed MWCNTs with transmission electron microscopy (TEM) revealed webs of long strings of crystallites, ~2-20 nm in diameter, in locations occupied initially by nanotubes. High-resolution TEM, selected-area electron diffraction, and convergent-beam electron diffraction techniques were used to identify the lattice structures of these carbon nanocrystals as cubic diamond, cubic n-diamond, lonsdaleite (hexagonal diamond), and a new carbon allotrope with face-centered cubic symmetry and lattice parameter a = 0.426 nm. This H-induced transformation was observed over the temperature range from 300 K to 1073 K, and investigated as a function of atomic hydrogen dose. Combining synergistically our experimental findings with molecular-dynamics simulations and first-principles density functional theory calculations, we show how H atoms produced in the dihydrogen plasma can induce sp2-to-sp3 C-C bonding transitions in MWCNTs and help nucleate various crystalline carbon allotropes such as cubic diamond and lonsdaleite.

### 9:00am **PS1-WeM4 Clarification of Surface and Interface Structures Exposed to Inductively Coupled Plasma with Various Superposed Bias Frequencies and Its Implication in Plasma Damage Control**

***Y. Nakakubo****, A. Matsuda, Y. Ueda, H. Ohta, K. Eriguchi, K. Ono*, Kyoto University, Japan

Plasma-induced Si substrate damage has become one of the critical issues in advanced MOSFETs with shallower junction in source/drain extension regions, since the damaged layer thickness will be in conflict with the device design margin (e.g. ~ 5 nm in 32-nm-node). The thickness is considered to be governed by plasma parameters such as ion energy distribution function (IEDF). With regard to plasma design, a plasma source driven by superimposed dual bias frequency was reported to control IEDF. For understanding the mechanism and suppressing the damage, the plasma-induced defects should be quantitatively estimated, and then, plasma should be optimized. We have preliminary quantified the damage induced by an inductively coupled plasma (ICP) reactor with superposed bias configuration by a photoreflectance spectroscopy (PRS)–based method.[1] Silicon wafers were exposed to an ICP reactor which apply bias powers with various superposed bias configurations with frequencies of 13.56 MHz and 400 kHz. The defect site density was determined by the PRS-based method. The surface and interface layers were assigned by spectroscopic ellipsometry (SE) and TEM. The surface layer growth and interfacial layer (IL) structure were studied by molecular dynamics (MD) simulation developed for the present process condition. The above structures were analyzed by stretching of capacitance-voltage (C-V) curves for the damaged samples. Based on the above comprehensive analyses, we found that an accurate model for plasma-damaged silicon surface structures should include an interface layer between the surface layer and the substrate, i.e., a conventional methodology can lead to an erroneous conclusion in addressing the structures. This bi-layer structure (surface stoichiometric $SiO_2$ and IL) was clarified by TEM, MD simulation and C-V test. The IL thickness increases with self-dc bias voltages. We also observed surface sputtering process (the decrease in surface layer thickness) and more severe damage at higher dc-bias voltages ( > 150 V), resulting in larger defect density (~ $10^{13}$cm$^{-2}$) in IL. Furthermore, it was quantitatively confirmed from PRS, SE and C-V techniques that interfacial layer growth and defect generation process depend on the superposed bias configurations with the same power. Quantitative measures and consideration of IL are key to future plasma and device designs.

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@super 1@Y. Nakakubo et al., Proc. Symp. Dry Process (2007) 287.

### 9:20am **PS1-WeM5 Studying Surface Damage during Dry Etching of Si(100) with Optical Second-Harmonic Generation in an $Ar^+/XeF_2$ Beam Setup**

***P.M. Gevers****, J.J.H. Gielis, H.C.W. Beijerinck, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

Increasing demands due to miniaturization in the semiconductor industry continuously lead to new challenges for plasma-based dry etching. Fundamental studies help to address these challenges, e.g., by clarifying the etching dynamics on the microscopic level. Circumventing the complexity of etching plasmas by using a multiple-beam experiment, we have investigated etching of the archetypical model system of Si(100) with $Ar^+$ ions and F radicals using $XeF_2$. The surface and interface-sensitive nonlinear optical technique of second-harmonic generation (SHG) was applied to gain insight into surface related processes such as the creation of a damaged layer as well as surface defect states involving strained Si-Si bonds and Si dangling bonds. The fundamental radiation for the SHG experiments was created by an optical parametric amplifier (80 MHz, 90 fs, 0.8-1.1 eV) pumped by the regenerative amplified radiation of a Ti:sapphire oscillator. Clean H terminated Si(100) samples were exposed to well characterized beams of low energy $Ar^+$ ions (70-1000 eV) and/or $XeF_2$ radicals. During exposure to $Ar^+$ ions the near surface region of the c-Si was essentially converted to an amorphous layer creating a two-layer structure. The studies were performed both spectroscopically during steady state conditions and in real time under transient conditions. Previous experiments,[1,2] in the 1.3-1.8 eV energy range yielded two spatially separated contributions with a 2ω resonance around 3.4 eV associated with modified Si-Si bonds, one at the a-Si surface and one at the a-Si/c-Si interface. The present interpretation for the 0.8-1.1 eV range indicates that the main part of the SHG signal arises from the tail of those resonances, which are assigned to $E'_0/E_1$-like transitions. A simple exponential model for the real-time data shows that a third contribution is necessary to describe the data well. This third contribution appears to be temporary, i.e., it is only present during the build-up of the a-Si layer. It will be discussed that this temporary contribution might be associated to the creation of dangling bonds and it will be addressed how it yields insight into the development of the a-Si layer over time.

[1] J.J.H. Gielis et al., Phys. Stat. Sol. (C) 2, 3968 (2005)

[2] J.J.H. Gielis et al., Phys. Rev. B 74, 165311 (2006).

### 9:40am **PS1-WeM6 Ion Induced Etching Reaction of $SiO_2$ and Si by $CF_3^+$ Irradiation**

***K. Karahashi****, S. Hamaguchi*, Osaka University, Japan

Fluorocarbon plasmas have been widely used to etch a silicon dioxide in the fabrication of semiconductor devices. In the view of the development of integrated semiconductor devices, more precise control of the etching process is required for further progress. In the previous work, the etching yield of SiO2 by CFx+ irradiation.[1] In the present work, we report measurement results of the desorbed products of SiO2 and Si etching due to the irradiation of CF3+ ions, which are considered to be the main ion species in fluorocarbon plasmas. Time of flight(TOF) measurements are also reported, which determines kinetic energies of the products. The low-energy mass-analyzed ion beam apparatus consists of an ion beam source, an ultra high vacuum scattering chamber. Various ions were generated in arc plasma of CF4 and were extracted from the ion source. CF3+ ions for

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* PSTD Coburn-Winters Student Award Finalist

sample irradiation were selected with a mass-analyzing magnet, passed through conventional beam optics, and decelerated to specified irradiation energy just before they reached the sample. Angular distribution of desorption products were detected through an aperture by a rotatable quadrupole mass spectrometer. To measure time of flight distributions of desorbed products, the ion beam is electronically chopped at deflectors in beam line When a CF3+ ion at 500 eV impinged on a SiO2 surface, the major desorbed product was SiF2. Angular distribution of SiF2 follows a cosine law, and the flux of SiF2 does not depend on the ion incident angle. On the other hands, When a CF3+ ion impinged on a Si surface with a large incident angle, the major desorbed product was Si and SiF. Angular distribution of desorbed Si and SiF strongly depends on the ion incident angle and energy. These results clearly show that the desorption process of etching on SiO2 differs from that on Si surface; collision cascades by incident ions on a surface hardly affect desorption of SiF2 from SiO2, unlike the desorption of Si atoms. This explanation of the desorption mechanism is also supported by the observation of TOF distribution measurements of desorbed SiF and SiF2. The TOF spectra of SiF and SiF2 are fitted well by collision cascade and Maxwell-Boltzmann distributions. These results indicate that the main desorption paths of SiF and SiF2 are different; SiF desorbs with collision cascade and SiF2 desorbs with thermal activation after collision cascade.

[1] K.Karahashi et al. J.Vac.Sci.Technol. A, 2004, A22, 1166.

### 10:40am **PS1-WeM9 Enhanced Ground and Metastable Atom Densities in Ar Diluted $N_2$ ICP for Nitridation of Hf Silicate**, ***T. Kitajima***, *T. Nakano*, National Defense Academy of Japan, *T. Makabe*, Keio University, Japan

The nitridation of high-k HfSiO film surface by nitrogen plasma is an important process for enabling amorphous homogeneous film without phase separation at high temperatures.[1] The relation of plasma generated species fluxes toward the film surface and the nitrogen incorporation degree of HfSiON is not well characterized. The authors have previously shown that the improved film quality of plasma grown $SiO_2$ due to rare-gas dilution of $O_2$ plasmas and its relation with the increased metastable $O(^1D)$ atom flux.[2] Here we diagnose the ground and metastable N atom densities in rare-gas diluted $N_2$ plasmas and relate the flux components with the N incorporation to the Hf Silicates. The ground $N(^4S)$ and metastable $N(^2D)$ density in the Ar diluted $N_2$ ICP (70 MHz) is measured by the VUV absorption spectroscopy using 120 nm and 149.3 nm emissions from the discharge light source ( $N(^4P) \rightarrow N(^4S)$ , $N(^2P) \rightarrow N(^2D)$). For the gas pressure of 100 mTorr and the ICP power of 100 W, $N(^2D)$ density is $2 \times 10^{10}$ $cm^{-3}$ in pure $N_2$ and decreases to $1 \times 10^{10}$ $cm^{-3}$ at $N_2/(N_2+Ar)$ ratio of 0.5 while $N(^4S)$ density stays at 7-8 x $10^{10}$ $cm^{-3}$. $N(^2D)$ density increases to $3.5 \times 10^{10}$ $cm^{-3}$ of maximum with the decrease of $N_2/(N_2+Ar)$ ratio to 0.1. The trend is also found for the case of He diluted $N_2$ plasma. The decrease of $N(^2D)$ for $N_2$ fraction of 100 to 50 % is due to the reduced dissociative excitation of $N_2$ while the EEDF is kept stable. The increase of $N(^2D)$ for $N_2$ fraction of 10 % is caused by the increase of high energy electrons due to the reduced energy loss by vibrational excitation of $N_2$. Since the $N(^2D)$ / $N(^4S)$ ratio reaches 0.5, we expect collisional excitation of $N(^4S)$ is important source for $N(^2D)$. The nitrided HfSiO films are examined by XPS and the N incorporation is correlated to the expected N atom flux to the surface. Detailed growth results are shown in the presentation.

Authors thank the Suzuki Foundation for the partial support of conducting this study.

[1] M.A.Quevedo-Lopez, J.J.Chambers, M.R.Visokay, A.Shanware, and L.Colombo, Appl.Phys.Lett., 87, 012902 (2005).

[2] T.Kitajima, T.Nakano, and T.Makabe, JVST A. (to be published).

### 11:00am **PS1-WeM10 Dependence of Carbon Removal Rate on the Structure of Porous Low-k SiOCH Films during $N_2/H_2$ Plasma Processes**, ***K. Kurihara***, Toshiba Corp., Japan

To realize highly reliable interconnects for sub 32 nm node LSI, low-k materials such as porous SiOCH films are demanded to be resistant to plasma processes, such as etching and ashing. This is because a methyl group which makes hydrophobic film is easily abstracted from the film during the plasma irradiation processes. We have examined the plasma resistance of SiOCH films which contained the methylene-bridge ($Si-CH_2-Si$) structure[1] using a plasma beam irradiation apparatus.[2] This apparatus enabled us to carry out plasma-surface interaction experimens using identified irradiation species. We used two kinds of spin-on-glass porous SiOCH films (k=2.0). One contained only methyl groups, and the other contained both methyl groups and methylene bridges. Used gas chemistry was nitrogen and hydrogen gas mixture plasma. We assumed the damage of the pattern sidewall and irradiated only neutral species from the plasma to the SiOCH films. Major irradiated neutral species were NHx (x=1-4) in addition to parent gases. We evaluated the damage of the film by using the decrease ratio of the carbon content measured as an index by XPS and FTIR. It was found that the decrease ratio of carbon in the SiOCH film contained only methyl groups was larger than that in the film contained methylene bridges. The authors thank JSR Corporation for supplying the SiOCH films.

[1] H. Miyajima et al. Proc. of Advanced Metallization Conf. 37 (2007).

[2] K.Kurihara et al. J. Vac. Sci.Technol. A 22, 2311(2004).

### 11:20am **PS1-WeM11 Mechanistic Influence of Substrate Temperature on the Plasma Deposition of Carbon Nitride Materials**, ***J.M. Stillahn***, *E.R. Fisher*, Colorado State University

In an effort to elucidate important processes involved in plasma-enhanced chemical vapor deposition (PECVD), our lab has employed several diagnostic tools to characterize the gas phase, film properties, and gas-surface interface under similar PECVD conditions. This work focuses on the application of these tools to the particular case of amorphous hydrogenated carbon nitride ($a-CN_x:H$) materials, which have a number of potential commercial applications. PECVD of $a-CN_x:H$ has been performed in inductively coupled rf plasmas using precursors that favor the formation of the CN radical, a likely contributor in the deposition process. CN was characterized in the gas phase using laser-induced fluorescence and mass spectrometry. Results suggest probable formation mechanisms and provide information about the energetics of the formed radicals. The imaging of radicals interacting with surfaces (IRIS) technique was used in these studies as a means of probing the behavior of CN radicals at the surface of the growing film under both ambient and heated-substrate conditions. These results, along with deposition rate and film composition data obtained as a function of substrate temperature, provide a more complete understanding of the interaction of plasma species with heated substrates in these systems.

### 11:40am **PS1-WeM12 Examining Plasma-Surface Interactions During Plasma Catalytic Removal of Atmospheric Pollutants**, ***M.M. Morgan***, *E.R. Fisher*, Colorado State University

Nitric oxide (NO) and sulfur dioxide ($SO_2$) are atmospheric pollutants that are produced from engine exhaust. Improvement in catalytic treatment of exhaust gases is therefore necessary to reduce these emissions. We are using plasma-catalytic processes to aid in the removal of pollutants from exhaust gases. An understanding of the fundamental chemical gas-phase and gas-surface processes is required to address this issue. With our imaging of radicals interacting with surfaces (IRIS) technique, we can simultaneously examine the gas-phase, perform surface analyses, and probe the gas-surface interface. IRIS combines laser-induced fluorescence and molecular beam techniques, thus we can probe a variety of important atmospheric species such as NO, $SO_2$, OH, CH, and CN. We have used IRIS to address the fundamental issue of NO and $SO_2$ removal by measuring relative gas-phase densities and by examining the steady-state surface reactivity of plasma-generated species on catalytic surfaces. For example, gas phase densities for NO demonstrate a significant decrease in NO at higher applied rf powers and when additives such as $H_2O$ and $CH_4$ are added to the system. Water has also been added to the gas mixtures containing NO and $SO_2$ to monitor the effect of OH production in these processes. Comparison of surface interaction data shows that NO scatters substantially whereas OH has a higher surface reaction probability. Substrates used include silicon wafers and a variety of catalytic surfaces such as Pt and Au. Additional optical emission spectroscopy and mass spectrometry data will also be presented on all of these systems. Preliminary IRIS data on CH and CN will also be included for comparison to NO, OH, and $SO_2$.

# Plasma Science and Technology
# Room: 306 - Session PS2-WeM

## Plasma Sources
## Moderator: E.A. Hudson, Lam Research, C.A. Wolden, Colorado School of Mines

### 8:00am **PS2-WeM1 Generating Short Wavelength Light from Compact Sources - Challenges and Applications**, ***W. Holber***, *S. Horne, M. Partlow, J. Silterra, D. Smith, J. Ye, H. Zhu*, Energetiq Technology, Inc. **INVITED**

Across a range of scientific and technological applications, there is a need for more capable short-wavelength light sources. In semiconductor manufacturing, critical dimensions are now in the nanometer range and EUV at 13.5 nm is under active investigation as a lithography source. In biotechnology, structural information on proteins requires UV down to 170 nm and internal cellular features are imaged using 2.3-4.3 nm radiation. Lasers can produce significant amounts of light at specific wavelengths in the UV, but do not provide broad wavelength coverage either in the UV or soft x-ray spectral regions. Synchrotrons are a source of bright, incoherent radiation at wavelengths from hard x-ray through DUV, but are based in large, centralized facilities. Incoherent light sources that are lab-based provide an alternative to synchrotrons in a growing number of applications. We will present results from a compact z-pinch plasma source customizable to different wavelengths in the EUV and SXR[1] range, generating up to 10 Watts of power at 13.5 nm, and a laser-driven lamp source of light from 170 to 800 nm. Both provide uniquely bright output over a range of applications.

[1] Work on SXR sources funded in part by NIH Grants 5R44RR022488-03 and 5R44RR023753-03.

8:40am **PS2-WeM3 3-Dimensional Model for Magnetized Capacitively Coupled Plasma Discharges**, ***S. Rauf***, *J.A. Kenney, K. Collins*, Applied Materials, Inc.

Static magnetic fields are often used in plasma processing systems to improve plasma confinement, modify plasma spatial profile or adjust other plasma characteristics. Aside from some simple magnetic field configurations, magnetized plasmas have a complex spatial structure and significant physics is missed in reduced (0, 1 or 2) dimensional models. A 3-dimensional fluid plasma model is used to understand the operation of magnetized capacitively coupled plasmas operating at 13.56 and 180 MHz in this paper. Both electropositive (Ar) and electronegative ($O_2$) gases are considered. To simplify interpretation of results, simulations have been done for an axi-symmetric reactor geometry. Static magnetic field is generated using current carrying wires, where several wire configurations that generate converging, diverging and uniform magnetic fields in the plasma region are considered. Our 3-dimensional plasma model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential, A, are solved in the frequency domain after each cycle for multiple harmonics of the driving frequency. The coupled set of equations governing the scalar potential, $\varphi$, and drift-diffusion equations for all charged species are solved implicitly in time. The model also includes the electron energy equation, Kirchhoff equations for the external circuit, and continuity equations for neutral species. The effect of static magnetic field is included through the charged species transport properties, which become tensor quantities in the presence of a static magnetic field. Without magnetic field, electron density peaks in the center of the chamber when the plasma is generated using a 180 MHz source. The 180 MHz plasma is also symmetric because of considerable distance from the chamber walls. When a static magnetic field parallel to the electrodes is applied, ExB drift in the sheath regions shifts the peak in plasma density off-axis. As the 180 MHz plasma is symmetric, ExB drift occurs in opposite direction in the two sheaths, which leads to an overall shearing of the plasma. Electron density peaks near the electrode edges in the 13.56 MHz plasma and the plasma is highly asymmetric. Application of magnetic field and the resultant ExB drift lead to overall shifting of the low frequency plasma in the ExB direction.

9:00am **PS2-WeM4 Effects of Very High Frequency Source Mixing and Inter-electrode Gap on Plasma Characteristics**, ***K. Bera***, *S. Rauf, K. Ramaswamy, K. Collins*, Applied Materials, Inc.

Capacitively coupled plasma (CCP) discharges are widely used for dielectric etching in the semiconductor industry. Very high frequency (VHF) power sources are being employed to generate plasmas for dielectric etching due to VHF's various benefits including low plasma potential, high electron density, and controllable dissociation. Electromagnetic effects tend to make the spatial and temporal behavior of VHF plasmas complex with a rich set of new physics. If plasmas are generated using multiple VHF sources, one can expect interaction between the sources and plasma characteristics to be different from those due to individual frequencies. We investigate the effects of VHF frequency mixing on plasma characteristics in this presentation. The study is done for a range of inter-electrode gaps. Both computational modeling and experiments are utilized. Our plasma model includes the full set of Maxwell equations in their potential formulation. The equations governing the vector potential are solved in the frequency domain after every cycle for multiple harmonics of the driving frequency. Current sources for the vector potential equations are computed using the plasma characteristics from the previous cycle. The coupled set of equations governing the scalar potential and drift-diffusion equations for all charged species are solved implicitly in time. Plasma simulation results show that electron density is usually higher in the center of the chamber at high frequencies due to a standing electromagnetic wave. Electrostatic effects at the electrode edges tend to get stronger at low VHF frequencies. Electron energy distribution function (EEDF) appears to be two-temperature Maxwellian. Ion saturation current measurements using a Langmuir probe show that ion saturation current, and hence plasma density, peaks in the chamber center at high VHF frequencies. As power at low VHF frequencies is added, ion saturation current increases at the edge of the electrodes and electrostatic effects become stronger. Even at high VHF frequencies, inductive heating at the electrode edges becomes strong for small inter-electrode gaps. This tends to increase electron density at electrode edge relative to the chamber center. As the gap is increased, the plasma is able to diffuse to the chamber center. The electromagnetic effects that dominate near the chamber center become more important than electrostatic effects.

9:20am **PS2-WeM5 The Impact of Electrode Gap and Gas Injection on Plasma Etch Uniformity**, *G.M. Amico*, ***M. Block***, *S. Sirard, J. Guha, A. Leming, A. Marakhtanov, E.A. Hudson, M. Srinivasan*, Lam Research

At the 32nm node and below, etch rate and CD uniformity requirements for multi-layer low k dual damascene integration schemes continue to tighten. Additionally, more focus is being placed on the process uniformity at the outer 5mm of the wafer. This paper examines the effect of electrode gap and the distribution of gas injection in a capacitively coupled reactor with confined plasma and adjustable gap. Radial etch rate and CD uniformity were studied for different films, with emphasis on multi-layer DD integration schemes. Mechanisms for the influence of electrode gap on process uniformity are different for ion limited and neutral limited etch regimes. Oxide etch rate radial uniformity as a function of gap shows a correlation to ion flux measurements. Narrower gaps tend to increase edge etch rates for all films, but the gap for optimal uniformity is dependent upon film composition. For multi-layer processing, the overall uniformity can be improved by employing different gap settings for each process step.

9:40am **PS2-WeM6 2 m Long-Line Plasma Production by Evanescent Microwave in a Narrowed Rectangular Waveguide**, *H. Shindo*, ***Y. Kimura***, Tokai University, Japan

Long line-shaped plasmas are inevitable in material processing in manufacturing industries, such as flat panel displays (FPDs) and surface modification of large- area thin films. In this work, we studied a newly proposed method of large-scaled line plasma generation. In this method, microwave power of frequency of 2.45 GHz in a narrowed and flattened rectangular waveguide is employed to produce plasma. Since the width of waveguide is very close to the cutoff condition, the wavelength of microwave inside the guide is very much lengthened, providing a condition of long uniform line plasma generation. The narrowed rectangular waveguides of 1.5 and 2.0 m in length and 5mm in height were examined. The width of the waveguide could be varied from 59 to 61 mm. The waveguide has a long slot of 5 mm width on the top surface to launch the microwave into the discharge plasma chamber. The plasmas of Ar nad He at the pressures of 0.1 to 5Torr were generated by employing an extremely long microwave wavelength. It was observed that the microwave electric field became more uniform as the wave guide width was narrowed, indicating that the plasma production is due to the mechanism expected. The optical emission line measurements in Ar and He plasmas also confirmed that the uniform plasma was produced in the entire region of 1.5 m and 2.0 m. The probe measuremnts of the plasma were also made, indicating that the plasma uniformity was within 10 % in the entire plasma. Thus we conclude that the present method of plasma production is quite advantageous for large area processing. Plasma extraction was also successfully tested.

10:40am **PS2-WeM9 Development and Characterization of a Radical Beam Source Based on Surface Waves for Plasma-Surface Reaction Studies**, ***R. Khare***, University of Houston, *L. Stafford*, Université de Montréal, Canada, *J. Guha, V.M. Donnelly*, University of Houston

Previously, we studied recombination of Cl and O on plasma-conditioned anodized aluminum and stainless steel surfaces. Cl and O atoms formed in chlorine or oxygen plasmas impinged on a cylindrical substrate that was rapidly rotated such that points on the surface were exposed to the plasma and then to a differentially-pumped analysis chamber equipped with either an Auger electron spectrometer or a mass spectrometer. Langmuir Hinshelwood (LH) recombination was observed by monitoring desorption of $Cl_2$ and $O_2$ with the mass spectrometer or through a pressure rise. In these previous experiments, however, Eley Rideal (ER) recombination (if it occurs) could not be detected because it would take place instantaneously in the presence of atom flux, and hence would cease as soon as the sample left the plasma. To observe the ER component, as well as to isolate LH recombination in plasmas with multiple radical species (i.e. most plasmas), a separate radical beam source is needed in combination with the plasma and spinning substrate. With this in mind, we investigated a surface-wave chlorine plasma operating at 2.45 GHz and sustained in a 8 mm O.D. quartz tube using a gap-type surfatron wave launcher. With added traces of rare gases, optical emission spectroscopy was used to measure Cl and $Cl_2$ densities and the electron temperature, $T_e$, at 50 mTorr as a function of distance from the wave launcher. The Cl(792.4 nm)-to-Xe(828 nm) emission intensity ratio, reflecting the Cl number density, decreased with distance from the launcher, while the $Cl_2$ (306 nm)-to-Xe emission ratio that is proportional to $Cl_2$ number density, peaked near the launcher. The $Cl_2$ percent dissociation obtained from the calibrated $Cl_2$ -to-Xe emission ratio was very high (97 %) near the launcher, and remained high (89 %) until the end of the plasma column (about 12 cm from the launcher for an absorbed power of 90 W). By selecting Ne, Ar, Kr, and Xe lines excited from the ground state which are characteristic of the high energy portion of the electron energy distribution function (particularly Ne), we found that $T_e$ increased from 5 to 10 eV as the observation point was moved away from the launcher. On the other hand, a nearly constant value of $T_e = 3.1 \pm 0.6$ eV was obtained using Ar, Kr and Xe lines excited to a significant extent through impact with lower energy electrons. Mechanisms for such high energy tails will be discussed.

11:00am **PS2-WeM10 Production-Worthy Pulsed ICP Plasma Processes**, ***S. Banna***, *V. Todorow, K. Ramaswamy, A. Agarwal, S. Rauf, K. Collins*, Applied Materials, Inc.

The transition to 45nm and smaller technologies has triggered intensive research effort among academic and industrial communities in search of wider range of plasma operating conditions aiming to improve etch processes for finer features. Pulsed radio frequency (PRF) plasmas are promising to achieve such a goal. It has been demonstrated through numerical modeling and basic experimental studies that PRF plasma might exhibit higher selectivity, improved uniformity, and minimal charge damage in many etch processes. However, due to the lack of efficient RF power delivery, PRF has only been utilized in a limited number of large-scale commercial applications. Particularly, two main PRF regimes were utilized in inductively coupled plasma (ICP) reactors. In the first, the source operates in the continuous wave (CW) RF mode while the bias operates in the PRF mode. In the second, the source power is pulsed while having the bias operating in the CW mode. The main challenge has been to minimize the amount of reflected power. Specifically, high bias reflected power was observed for low-pressure processes with source pulsing, in which time-modulation of the source power is highly coupled to the bias. The high reflected power is mainly due to the mechanical nature of conventional dynamic matching networks used to reduce the reflected power. The response time of the mechanical adjustment is of the order of hundreds of milliseconds. Hence, the match cannot track the changes in the time-modulated power as the pulse frequencies of interest are greater than 1kHz. There is a vital need for new capability to reduce the reflected power in sub-millisecond time scale. Recently, we have developed production-worthy, reliable and robust PRF plasma operation in a commercial ICP reactor that provides an expanded window of operation by establishing multiple techniques for optimizing RF power delivery in PRF mode. By so doing the matching response time is reduced to as low as a few microseconds. Accordingly, larger number of etch processes operating at pulsed plasma mode are feasible. The robustness of the system is manifested by its ability to provide a variety of RF modes of operation, furnishing more flexibility in etch processes design. By utilizing these modes in ICP reactor, it was demonstrated that one can improve uniformity, enhance selectivity and eliminate micro-trenching in real production etch processes. Supporting plasma modeling and diagnostics will be discussed.

## Advanced Surface Engineering
## Room: 204 - Session SE-WeM

## Atmospheric Pressure Treatments and Hard and Nanocomposite Coatings

**Moderator:** H. Baránková, Uppsala University, Sweden, P.H. Mayrhofer, Montanuniversität Leoben, Austria

8:00am **SE-WeM1 Controlling Plasma Deposition with Liquid Aerosol Precursors**, ***L. O'Neill***, *J.D. Albaugh*, Dow Corning, Ireland **INVITED**

Recent studies have clearly demonstrated that numerous precursors can be used to produce thin film coatings by injecting liquid aerosol droplets into a non-thermal equilibrium atmospheric pressure plasma. The deposition appears to proceed via a controlled free radical polymerisation with controlled precursor fragmentation. It has recently been reported that several different siloxane products and intermediates can be used to prepare thin films by this method and the resultant coatings can be tailored to produce deposits which vary from hydrophobic siloxane to cross-linked silica thin films. Linear, cyclic, dimethyl and Si-H containing siloxanes have been deposited with equally high deposition rates. However, under certain conditions, coatings deposited from linear and dimethyl structures can appear "wet" and have a presumably low cross-link density compared to their cyclic or Si-H counterparts. Therefore, a more detailed study has been undertaken to investigate which factors control deposition rate and cross-link density in liquid aerosol – plasma polymerisation processes. A series of liquids have been nebulised and introduced into a purpose built RF atmospheric pressure plasma jet operating with helium as the main process gas. The resultant coatings have been thoroughly characterised to determine which chemical properties of the precursor directly impact upon the chemistry and morphology of the coatings.

8:40am **SE-WeM3 Deposition of Metallic Nanoparticles using Atmospheric Plasma**, *F. Demoisson,* Universite Libre de Bruxelles, Belgium, *J.J. Pireaux,* Facultés Universitaires Notre Dame de la Paix, Belgium, *H. Terryn,* Vrije Universiteit Brussel, Belgium, ***F. Reniers***, Universite Libre de Bruxelles, Belgium

The deposition of metal nanoparticles on various substrates is of high interest in surface science, as they can induce new chemical properties on surfaces. Applications can be found in catalysis, for gas sensor applications, in environmental science,.... however, the deposition of metal nanoparticles is facing many challenges such as : difficulty to have a strong binding on various surfaces (polymer, carbon, glass,...), technological difficulty of the deposition process, bad dispersion of the particles on the surface, bad particle size distribution,.... Usual processes require today high vacuum evaporation of the metal onto preactivated surfaces, or the use of hazardous organometallic compounds as precursors. In this work we present a new process[1] to deposit, in one step, easily, metal nanoparticles (Au, Rh, Pt) onto various surfaces (HOPG, glass, polymer, metal), using an atmospheric plasma torch (AtomFlo, SurX Technologies). The resulting surfaces are characterized by FEG-SEM and XPS. The results show an excellent particle size distribution, and a very good homogeneity of the particle distribution on the surfaces. Surface coverages in the range of 10-15% were obtained. The adhesion of the particles on the surface was tested using ultrasonication and proved to be very good.

[1] F. Demoisson, JJ Pireaux, F. Reniers, "process to deposit nanoparticles on a substrate" patent pending 08151463.0-1215.

9:00am **SE-WeM4 Design and Applications of the Atmospheric Pressure Hollow Cathodes**, *H. Baránková,* ***L. Bárdos***, Uppsala University, Sweden

The hollow cathode cold atmospheric plasma sources, similarly as hollow cathode plasma sources at the moderate and low pressures, exhibit the Hollow Cathode Effect (HCE). The atmospheric pressure, however, requires reduction of dimensions, so that a typical structure inside the hollow cathode, i.e. the space charge sheath - common negative glow - space charge sheath, is preserved. The experimental results on the hollow cathode generation, using a special construction with a tunable wall separation, are presented. The influence of the gas and the type of generation on the optimum size is investigated. The experimental results are supported by the hollow cathode model. The applications of the hollow cathodes operating at the atmospheric pressure are given.

9:20am **SE-WeM5 Advanced Atmospheric Pressure Microplasma Sources for Surface Treatment**, ***K.-D. Weltmann***, *R. Brandenburg, R. Foest, E. Kindel, M. Stieber, T.V. Woedtke*, Leibniz-Institute for Plasma Science and Technology e.V. (INP Greifswald), Germany **INVITED**

Compact miniaturized atmospheric plasmas exhibit very promising technological potential for surface treatment. Basically, there are two features which make them unique: (I) the tool-like, small size and light weight plasma generation unit allows fast and almost arbitrary 3D movements and (II) the contracted and comparably cold plasmas allow focused small-spot treatments, even of heat sensitive small size objects with temperature loads to the surface between 35°°C and 90°C. Especially in the area of biomedical applications these opportunities triggered significantly increasing research and development of plasma application directly to living objects. But also industrial surface treatment processes such as activation, functionalization, passivation, coating and etching gain importance. Here, an overview of different tailor-made miniaturized atmospheric pressure plasma sources is presented which can be used for specific purposes of surface coating, functionalization and decontamination. Actually, plasma assisted processes for biological decontamination up to the level of sterilization are becoming an alternative to conventional methods especially for heat sensitive materials. However, the realization of industrial plasma-based decontamination or sterilization technology still remains a great challenge. This is due to the fact that antimicrobial treatment processes needs to consider all properties of the product to be treated as well as the requirements of the complete procedure, e.g. a reprocessing of medical instruments. Here the applicability of plasma-based processes for the antimicrobial treatment on selected, heat sensitive products with special geometries is demonstrated. Modular and selective plasma sources, developed at INP are used which match the specific requirements of a variety of complex 3-dimensional structures. Measurements of relevant plasma properties (optical emission in the VIS, UV, and VUV region, along with substrate temperatures) are reported. Following this, a discourse is given about possible treatment processes and the state of the art in the new field of plasma medicine, i.e. about expected benefits of localized plasma treatment of living tissue for healing purposes. In the last part of the presentation the use of different RF-driven plasma atmospheric pressure microplasma-jets for deposition of dense SiO$_x$ films with potential for barrier layers will be described. Measurements of relevant film properties (chemical composition and morphology) are reported and the state of the art of an advanced source tuning regime named "locked mode" is described. This mode leads to improvements of film quality and lateral homogeneity in the deposition spot.

10:40am **SE-WeM9 Stress and Strain in Polycrystalline Thin Films**, ***G.C.A.M. Janssen***, TU Delft, The Netherlands **INVITED**

Polycrystalline thin films on substrates usually are in a "stressed" state. In the presentation the two main methods for stress measurements, wafer curvature and X-ray lattice parameter measurements will be presented. Special attention will be given to the information that can be obtained by applying both techniques. This discussion will be followed by a discussion of recent results on stress in hard polycrystalline films. For Cr and CrN films, it has been shown that the stress is not uniform over the thickness of the film. High tensile stresses are observed near the substrate-film interface. Lower tensile stresses are observed further away from the interface. Moreover, it has been shown that the tensile stress is generated at the grain boundaries. In the case for which the deposition of the film is accompanied by an ion bombardment, a compressive stress is generated. The tensile- and compressive stresses in these films are independent and additive. For TiN films the situation is even more complicated. For TiN higher compressive stresses are observed close to the substrate-film interface. This effect is explained form the observation that for TiN, the evolution of the grain boundary density is accompanied by an evolution of the texture. Various texture components exhibit a different sensitivity to compressive stress generation by ion-peening.

11:20am **SE-WeM11 The Location and Effects of Si in Arc-Evaporated (Ti$_{1-x}$Si$_x$)N$_y$ Thin Solid Films**, *A. Flink, M. Beckers, B. Alling, J. Bareno,* Linköping University, Sweden*, J. Sjölen,* Seco Tools AB, Sweden*, I. Abrikosov, **L. Hultman***, Linköping University, Sweden

Arc-Evaporated (Ti$_{1-x}$Si$_x$)N$_y$ thin solid films have been studied by analytical electron microscopy, X-ray diffraction, scanning tunneling microscopy, X-ray photoelectron spectroscopy, elastic recoil detection analysis, and nanoindentation. As-deposited films form cubic solid solutions with Si substituting for Ti up to x = 0.09. Si segregation in films with higher Si content, up to x = 0.20, results in a feather-like microstructure consisting of cubic TiN:Si nanocrystallite bundles with low-angle grain boundaries and a very high dislocation density of $10^{14}$ cm$^{-2}$ (corresponding to a cold-worked alloy). Correspondingly, N content in the films increases almost linearly with Si content from y = 1.00 for x = 0 to y = 1.13 for x = 0.20. Upon annealing at 1000 °C, films with Si contents between x = 0.04 and 0.20 develop a metastable crystalline SiN$_z$ ($1.0 \leq z \leq 1.33$) tissue phase, which is semicoherent to TiN. These films exhibit retained hardness between 31-42 GPa and are compositionally stable. Thus, superhard TiN-SiN$_z$ nanocomposites without amorphous silicon nitride phase can be produced by arc-evaporation and subsequent annealing. At 1100-1200 °C, the films soften due to amorphization of the SiN$_z$ tissue phase, followed by recrystallization of the TiN grains, and Si and N diffusion out of the film. Ab-initio calculations performed in parallel to these experiments reveal that c-Si$_3$N$_4$ can be stabilized with D0$_{22}$ or L1$_2$ ordered Si vacancies in a ZnS-like structure, in agreement with previous experimental results published by us,[1-3] while phonon calculations show that stoichiometric c-SiN is dynamically unstable in the NaCl and ZnS structures.[4,5]

[1] Hans Söderberg, Jon Molina-Aldareguia, Lars Hultman, and Magnus Odén, J. Appl. Phys. 97 (2005) 114327.

[2] Lars Hultman, Javier Bareño, Axel Flink, Hans Söderberg, Karin Larsson, Vania Petrova, Magnus Odén, J. E. Greene, and Ivan Petrov, Phys. Rev. B75 (2007) 155437.

[3] Hans Söderberg, Axel Flink, Jens Birch, Per O.Å. Persson, Manfred Beckers, Lars Hultman, and Magnus Odén, J. Materials Research 22 (2007) 3255.

[4] Axel Flink, PhD Thesis "Growth and Characterization of Ti-Si-N Thin Film" Linköping Studies in Science and Technology, Dissertation No. 1190, Linköping, Sweden (2008). www.ep.liu.se.

[5] B. Alling, E. I. Isaev, A. Flink, L. Hultman, I. A. Abrikosov, submitted.

11:40am **SE-WeM12 Phase Stabilization in CrN by Addition of Si and O**, *L. Castaldi,* EMPA, Switzerland*, D. Kurapov, A. Reiter,* OC Oerlikon Balzers AG, Switzerland*, V. Shklover,* ETH Zurich, Switzerland*, **J. Patscheider***, EMPA, Switzerland

The influences of adding silicon and oxygen during deposition of CrN by reactive cathodic arc evaporation on composition, structure, hardness and thermal stability were investigated. Both Cr-N-X phase ternary systems, where X denotes O or Si, exhibit a strong influence of X on hardness and thermal stability. Addition of these two elements leads to a decrease of the grain size of the cubic Cr-N-X phase, at the composition of optimum performance, down to a third or fourth of that of undoped CrN. XRD investigations suggest at least a partial substitution of N by O accompanied by the formation of an amorphous phase at higher O content, thereby forming a nanocomposite structure. The hardness of Cr-N-O coatings increases with increasing the oxygen content up to a value of 28 GPa, while fully oxidized Cr$_2$O$_3$ films showed lower hardness values around 12 GPa. The addition of Si resulted in a maximum hardness of Cr-N-Si of about 25 GPa. Cr-N-X coatings showed both an onset of oxidation which was promoted by about 200°C as compared to that of CrN. The underlying mechanisms, as evidenced by the performed measurements, will be discussed.

## 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. Sathiyanarayanan*, 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 O$_2$ and annealed to form order structures. The O$_2$ dosing pins the Fermi level at high local coverage. Formation of Ge-N adsorbates is more challenging since N$_2$ nor NH$_3$ 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 GeO$_2$.

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.

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

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

[3] P.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$^o$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.

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

[2] J. 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 $Ag_3S_3$.[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 $Ag_3S_3$ 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(2x8) reconstruction at room temperature. Au growth on Ge(111) above 300°C occurs via nucleation. The first layer is an epitaxial $(\sqrt{3}x\sqrt{3})R30°$ phase with a coverage of 1ML. Further Au coverage results in the formation of islands. When heated to about 620°C, the $(\sqrt{3}x\sqrt{3})R30°$ 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. Bussmann,* Sandia National Laboratories, *S. Bockenhauer,* 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$^o$ 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. Bennewitz, 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. Bennewitz, 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. zu 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 $LiNbO_3$(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 $LiNbO_3$(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 $LiNbO_3$(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 $LiNbO_3$ support, and annealing. In contrast, preliminary results suggest that Pd behaves very differently on negatively poled $LiNbO_3$. 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 $LiNbO_3$(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 depended of intrinsic domain nucleation for the first time using Piezoresponse Force spectroscopy of model oxide materials, $BiFeO_3$ and $Pb(Zr_{0.2}Ti_{0.8})O_3$ 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 fuels 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-stabalized-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 $Al_2O_3$/FeAl(110)**, ***M.C. Patterson****, O. Kizilkaya, R.L. Kurtz, P.T. Sprunger*, 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.

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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 $TiO_2$ 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 Tc 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 Accelarator 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 stablized MnCu surface alloy.

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

11:00am **SS2+NC-WeM10 Adsorption of the Thiol Molecule (SCH$_3$)$_2$ on a Metallic Quantum Well System**, ***L. Tskipuri***, *R.A. Bartynski*, Rutgers University

We have studied the bonding of the thiol molecule dimethyldisulfide (SCH$_3$)$_2$ 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?

## Thin Film
## Room: 302 - Session TF-WeM

## Chemical Vapor Deposition
### **Moderator:** P.D. Rack, University of Tennessee

8:00am **TF-WeM1 Growth and Functional Properties of Thin Film Oxides Synthesized under Photon Irradiation**, ***S. Ramanathan***, Harvard University **INVITED**

Thin film oxides play a key role in several advanced electronics and energy technologies such as alternate gate dielectrics, memory devices and functional membranes in energy generation. Developing novel routes for synthesis of oxide thin films with controlled structure and stoichiometry is therefore of great importance. In this talk, we will present experimental and modeling results from our on-going work on synthesis of ultra-thin oxides under photon irradiation with particular emphasis on structure-property relations. Model systems that will be discussed include ultra-thin fluorite-strucutred zirconia dielectrics synthesized by low temperature ultra-violet ozone oxidation and yttria-doped zirconia films grown by physical vapor deposition methods. The role of photon irradiation during oxide formation will be discussed in depth along with their impact on functional properties. Examples of applications of the processing technique in advanced electronic devices as well as solid oxide fuel cells will be presented.

8:40am **TF-WeM3 A Zone Diagram for Conformal Film Growth by CVD**, ***J.R. Abelson***, *A. Yanguas-Gil, N. Kumar, Y. Yang*, University of Illinois at Urbana-Champaign

The field of thin film growth using physical vapor deposition has benefited enormously from the mechanistic insights provided by Thornton's zone diagram, which he introduced to this society in 1974. There has been no direct analogue for the case of chemical vapor deposition (CVD), presumably due to the multiplicity of chemical reactions and the wide range of experimental conditions associated with the use of different precursor molecules. One major advantage of CVD is the ability to deposit films with extremely good conformal (step) coverage, which is a requirement for the additive fabrication of many current and proposed nanoscale devices. We show that all conformal CVD processes share certain kinetic requirements and limitations. Each of these can be represented on a plot of precursor pressure vs. substrate temperature: threshold phenomena, such as the onset temperature for reaction, appear as a vertical or horizontal line; kinetic competitions, such as surface adsorption vs. desorption, appear as exponential slopes. The properties of the precursor molecule and the aspect ratio of the feature to be coated (represented by a trench) then define a polygonal figure on the (P,T) plot which may or may not allow for conformal growth. We further show that many of the kinetic coefficients can be represented in normalized form, which we present as a zone diagram for conformal growth by CVD. The usefulness of this construction is illustrated by analyzing well-known experimental systems, such as W or $SiO_2$ growth, and the recent results we have obtained for the low temperature CVD of $HfB_2$, $CrB_2$, $TiB_2$ and MgO. For all these systems, the underlying mechanism that affords good step-coverage is surface site-blocking due to adsorbed precursor molecules or reaction byproducts or co-reactants. The experimental results are consistent with the predictions of the zone diagram. We conclude by showing how the site-blocking processes, and thus the degree of conformal coverage, can be controlled through the addition of site-blocking agents, such that a precursor that normally does not afford conformal growth can be transformed into one that coats very deep features.

9:00am **TF-WeM4 Conformal Chemical Vapor Deposition of Metal Oxide Thin Films using Metal-Diboranamide Precursors**, ***A. Yanguas-Gil***, *N. Kumar, S.R. Daly, Y. Yang, G.S. Girolami, J.R. Abelson*, University of Illinois at Urbana-Champaign

The N,N-dimethyldiboranamide (dmdba) ligand is used to synthesize a wide range of different alkaline earth, transition metal and rare earth metal compounds that have sufficient volatility to serve as precursors for the growth of complex materials by chemical vapor deposition (CVD). In this work, we report the successful growth of $TiO_2$, erbium-doped $TiO_2$, MgO, $Y_2O_3$, $La_2O_3$ and titanate complex oxides using water as a co-reactant at substrate temperatures as low as 225°C. The growth process is monitored in-situ using spectroscopic ellipsometry, and the films are characterized ex-situ by AES, RBS, SEM, XRD and AFM. The crystallinity of the films upon annealing is also studied. The results show that the metal center has a strong influence in the reactivity, surface chemistry and the vapor pressure of the precursor. The impurity concentrations in the films are below the AES and RBS detection limits, indicating that the dmdba ligand is efficiently released from the growth surface to the gas phase. Under suitable conditions the film growth is highly conformal, e.g. MgO films have been deposited onto trenches with 30:1 depth:width ratio with a step coverage (minimum to maximum thickness ratio) of 90%. The corresponding film growth rate is 5-100 times greater than that achievable using atomic layer deposition due to the uninterrupted nature of the CVD process. These results make the dmdba precursor family very attractive for the synthesis of complex oxide films by CVD.

9:20am **TF-WeM5 Chemical Vapor Deposition of $WN_xC_y$ using Tungsten Piperidylhydrazido Complex: Deposition, Characterization and Diffusion Barrier Evaluation**, ***D.J. Kim***, *O.H. Kim, T.J. Anderson, J. Koller, L. McElwee-White, C.L. Leu, J.M. Tsai, D.P. Norton*, University of Florida

The tungsten piperidylhydrazido complex $Cl_4(CH_3CN)W(NN(CH_2)_5)$ (designated as 1) was deposited by metal organic chemical vapor deposition (MOCVD) for growth of tungsten carbonitride ($WN_xC_y$) thin films in the temperature range 300 to 700 °C in the absence and presence of ammonia ($NH_3$). The effect of deposition temperature and $NH_3$ on the film microstructure, chemical composition, bonding states, growth rate, electrical resistivity, lattice parameter, and grain size were studied. The microstructure of films deposited with $NH_3$ was amorphous below 500 °C and polycrystalline at and above this temperature. The chemical composition of films deposited with $NH_3$ increased the nitrogen levels and decreased the carbon levels over the entire deposition temperature range as compared to films deposited without $NH_3$. The XPS results indicate that W is primarily bonded to N and C for films deposited at 400 °C, but at lower deposition temperature the binding energy of the W-O bond becomes more evident. Growth rates of films deposited with $NH_3$ varied from 0.6 to 4.2 Å/min. Diffusion barrier properties were investigated from $Cu/WN_xC_y/Si$ stacks consisting of 100 nm Cu deposited at room temperature by reactive sputtering on a $WN_xC_y$ film deposited at 400 °C by CVD. XRD patterns, AES compositional depth profiling, and cross-sectional TEM imaging were used to determine the performance of the diffusion barrier. $Cu/WN_xC_y/Si$ stacks annealed at 500 °C for 30 min maintained the integrity of both $Cu/WN_xC_y$ and $WN_xC_y/Si$ interfaces. Hence, $WN_xC_y$ thin films deposited at 400 °C are a viable material to serve as a Cu diffusion barrier to prevent interdiffusion and intermixing between Cu and Si. The film properties of thin films deposited with 1 and tungsten imido complexes $Cl_4(CH_3CN)W(NR)$ (R = Ph, $^i$Pr, and allyl)[1] were also compared to provide insight into the effect of hydrazido and imido ligands on film properties.

[1] O. J. Bchir, K. M. Green, H. M. Ajmera, E. A. Zapp, T. J. Anderson, B. C. Brooks, L. L. Reitfort, D. H. Powell, K. A. Abboud, L. McElwee-White, J. Am. Chem. Soc. 127 (2005) 7825-7833.

9:40am **TF-WeM6 Conformality of Chemical Vapor Deposited Copper Oxide Thin Films in High Aspect Ratio Features for ULSI/MEMS Applications**, ***Y. Shimogaki***, *Y. Susa*, The University of Tokyo, Japan

Kinetics of chemical vapor deposition of copper oxide ($Cu_2O$) thin film using Cu(tmvs)(hfac) and $H_2O_2$ as precursors were investigated. $Cu_2O$ films could be deposited at relatively low temperature, as low as 80°C, on various kinds of under-layers including thermal silicon oxide and TaN. $Cu_2O$ films can be easily reduced to metallic copper thin films using formic acid (HCOOH) as reducing agent. This reduction process can be performed at low temperature of around 100°C. Thus, $Cu_2O$ deposition and its reduction process combination can be a novel chemical route to make metallic copper film at low temperature. In this work, we examined the source precursor partial pressure dependencies of $Cu_2O$ growth rate (G.R.) using cold wall type CVD reactor. G.R. showed non-linear behavior, know as Langmuir-Hinshelwood mechanism, against partial pressure of Cu precursor ($P_{Cu}$), while G.R. showed linear dependence against the partial pressure of $H_2O_2$ ($P_{H2O2}$). These kinetics suggest $Cu_2O$ is formed via direct reaction of gas-phase $H_2O_2$ and adsorbed Cu precursor. The extendibility of this $Cu_2O$-CVD process to make conformal deposition onto high aspect ratio (HAR) features was systematically investigated. The film thickness profile within HAR-feature, like as trench, was analyzed by solving diffusion equation for precursor molecules. The consumption of the precursors by surface reaction, whose rate had been obtained from the above mentioned kinetic studies, was taken into account. The analysis suggested that film thickness non-uniformity was mainly derived from the consumption of $H_2O_2$. The Cu precursor concentration profile does exist in the HAR-features, however, due to the non-linear kinetic behavior of G.R. against $P_{Cu}$, its non-uniformity will not affect to the film thickness uniformity. Existence of gas-phase reaction to decompose $H_2O_2$ was also confirmed from the growth rate profile analysis. These kinetic information were integrated and extendibility of this $Cu_2O$-CVD process for conformal deposition onto HAR features was estimated. We could conclude that this process is suitable for ULSI interconnect and TSV applications with nearly 100% step coverage, but for MEMS applications, this process may have a limit. Step coverage of about 40% or less will be obtained for aspect ratio of 100, which may be sometimes required for MEMS applications.

10:40am **TF-WeM9 Structure and Morphology of Pentacene Film Grown on HOPG**, ***J. Götzen***, *D. Käfer, Ch. Wöll, G. Witte*, Ruhr-University, Germany

Previous studies have shown that the structure of organic semiconductor film depends sensitively on the interaction with the substrate. In this respect we have studied the film growth of pentacene onto highly oriented pyrolytic graphite which constitutes an interesting model system for a chemically rather inert but - in contrast to amorphous oxides – highly ordered crystalline substrate. Here we report a comprehensive characterization of the microstructure, morphology and thermal stability of pentacene films grown by OMBD onto freshly cleaved HOPG by employing STM, AFM, NEXAFS, XRD and TDS. Despite a rather weak, essentially van-der Waals-type substrate interaction pentacene molecules adsorb with their planes oriented parallel to the surface and form a commensurate monolayer due to the close match of the molecular carbon frame and the underlying graphite lattice. This packing motive, however, is not maintained in multilayer films where instead molecules in subsequent layers are tilted around their long axis. The multilayer growth is further characterized by the formation of individual crystalline islands exhibiting the Siegrist bulk polymorphism for rather different growth conditions (rate and temperature) and thus parallels the growth scenario observed previously for pentacene on Au(111)[1] In contrast films with upright oriented molecules were obtained if the graphite had been briefly sputtered before deposition and thus emphasizes the importance of micro-roughness on the resulting film growth.

[1] D. Käfer, L. Ruppel, G. Witte, Phys. Rev. B 75, 085309 (2007).

11:00am **TF-WeM10 Electrically Controllable Stationary Hadamard Shutter Exploiting the Semiconductor-To-Metallic Phase Transition of W-doped $VO_2$ Arrays**, ***M. Soltani***, *M. Chaker*, INRS-Énergie, Matériaux et Télécommunications, Canada, *E. Haddad, R.V. Kruzelecky, W. Jamroz*, MPB Communications Inc., Canada, *J. Margot*, Université de Montréal, Canada, *P. Laou, S. Paradis*, Defence R&D Canada-Valcartier

The well-known transmitting semiconductor (on) to the reflecting metallic (off) phase transition (SMT) of thermochromic $VO_2$ can be controlled by external parameters such as temperature, pressure, photo-carrier injection, photo-excitation, and an electric field. Also, the transition temperature (about 68 °C) of $VO_2$ can be controlled by metal doping such as W, Ti, Al, Mo, etc. Undoped and doped-$VO_2$ smart coatings are thus excellent materials for various switching applications such as IR uncooled bolometers, smart windows, all-optical, electro-optical and microwave switching devices. Here, we exploit the SMT characteristic of W(1.4 at. %)-doped $VO_2$ active layer in the fabrication of stationary Hadamard shutter arrays. The active layer was synthesized by reactive pulsed laser deposition. The micro-optical active slits were patterned by photolithography followed by plasma etching, while the lift-off process achieved the Au/NiCr electrodes onto the top of the individual micro-slit. This shutter consists of 16 active planar micro-optical slits for which both the infrared transmittance and reflectance switching can be controlled individually at room temperature by an external voltage. This allows performing any desirable on-off switching combinations. Both the electroreflectance and electrotransmittance switching of the individual slits were investigated at 1.55 μm. The transmittance switching was as high as 25 dB, while the reflectance switching was about 6 dB. In addition, the electrotransmittance switching modulation (on/off) was demonstrated at 1.55 μm by switching the individual slits by an external ac signal. This shutter can be used as individually programmable 16 multi-entrance slits (i.e., stationary Hadamard shutter) instead of the traditional single entrance slit of dispersive IR spectrometers. Thus, the role of the Hadamard shutter consists of multiplexing the incoming information into the output detector element arrays using binary coding. As results, enhancement of the signal-to-noise ratio and improvement of both the sensitivities and the resolutions of these spectrometers.

11:20am **TF-WeM11 Molecular Beams Tunable in Energy Yield Novel Growth Behavior in Small-Molecule Organic Semiconductors**, ***A. Amassian***, *S. Hong, T.V. Desai,* Cornell University, *S. Kowarik,* University of California at Berkeley, *J.E. Goose, A. Papadimitratos, V.A. Pozfin,* Cornell University, *A.R. Woll, D.M. Smilgies,* Cornell High Energy Synchrotron Source, *F. Schreiber,* Universität Tübingen, Germany, *P. Clancy, G.G. Malliaras, J.R. Engstrom*, Cornell University

The performance of organic electronic devices is closely tied to the packing structure and morphology of molecular semiconductors at the semiconductor-insulator interface, which in turn are intricately linked to molecular-scale processes operant during thin film growth. Tunable supersonic molecular beams have emerged as a versatile method to manipulate the state of incident molecules (e.g., kinetic energy, vibro-rotational states) and to promote novel growth behavior on the surface of the insulator (i.e., $SiO_2$). The growth of small-molecule thin films of pentacene and diindenoperylene from molecular beam sources tunable in kinetic energy (1 to 10eV) and flux was investigated in situ using synchrotron-based time-resolved X-ray reflectivity and grazing incidence X-ray diffraction techniques and ex situ by non-contact atomic force microscopy. Time-resolved X-ray scattering experiments reveal significant acceleration of the growth rate between the submonolayer and the multilayer thickness regimes. The acceleration of growth rate is not observed in thermal processes; it is operant when molecules are incident at hyperthermal kinetic energy and further enhanced by increasing the energy of molecules. Rate equation modeling of X-ray reflectivity data suggests that small-molecules incident at hyperthermal kinetic energy are trapped much more efficiently by a molecular monolayer formed on the surface of the "hard" insulator than by the bare insulator itself. Molecular dynamic simulations reveal that energetic molecules undergo a so-called "soft-landing" on molecular monolayers, during which can insert the molecular layer near step edges and transfer most of their kinetic energy to the "soft" molecular layer. Organic thin film transistors of pentacene and diindenoperylene fabricated from molecular beams tunable in energy exhibit significant increases – by a factor of five for pentacene and by an order of magnitude for diindenoperylene – of the field effect mobility in conditions of high kinetic energy. The relationship between the kinetics of growth and improved charge transport characteristics of conjugated small-molecule semiconducting thin films is discussed.

11:40am **TF-WeM12 Vanadium Oxide Thin Films for IR Imaging Bolometric Applications Deposited by Reactive Pulsed DC Sputtering**, ***N.M. Fieldhouse***, *S.S.N. Bharadwaja, M.W. Horn, S.M. Pursel, R. Carey*, Pennsylvania State University

Uncooled infrared focal plane arrays (IRFPAs) are the critical technology for night vision cameras needed for military and civilian applications. The two most widely used temperature sensitive imaging materials are vanadium oxide and amorphous silicon typically deposited by reactive ion beam sputtering and PECVD respectively. In this work, we report on vanadium oxide (VOx) films deposited by a reactive pulsed DC magnetron sputtering process using a pure vanadium metal target that are comparable to those presently used in commercial IRFPAs. The structural, microstructure and electrical properties were evaluated as a function of processing parameters such as substrate temperature, range of oxygen to argon ($Ar:O_2$) partial pressures ratio, and pulsed DC power. The VOx films deposited at various substrate temperatures between 30-400 °C over a range of $Ar:O_2$ partial pressure ratios exhibited distinct variations in their microstructure even though most of them appear amorphous using glancing angle X-ray diffraction. The critical electrical properties such as the temperature coefficient of resistance (TCR), resistivity and noise levels were found to be sensitive to film microstructure. Thin films of VOx (50-200 nm) were deposited with resistivity values between 0.1-100 ohm-cm and a TCR in the range of -1.1% to -2.4% $K^{-1}$. In particular, films grown at lower substrate temperatures with higher oxygen partial pressures have shown finer columnar grain structure and exhibited larger TCR and resistivity.

## 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 models[2] 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. Rezvanian, 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/nanoadhesion 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 a octadecytrichlorine 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. Rezvanian, 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.

[1] Hook, 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

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

[3] Asay, 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 contract properties such as adhesion and friction. Water adsorption can causes 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.

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

[2] J. 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.

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

### 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).

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-WeM

## Exhibitor Workshops
**Moderator:** R.A. Childs, MIT

10:00am **EW-WeM1 New Premium Line of Turbomolecular Pumps by Oerlikon Leybold Vacuum, TURBOVAC SL 80 - 300 – 700***, M. Sydow,* ***B. Rock***, Oerlikon Leybold Vacuum

Oerlikon Leybold Vacuum as a leading supplier of vacuum technology with the largest product offering has recently introduced the new premium line of turbomolecular pumps, the TURBOVAC SL line. This family has been developed to generate high vacuum in the most economic way for most simple operation. The pumps are available in models with pumping speeds of 70 to 700 l/s generated by computer designed rotor devices. The high precision mechanical ball bearing systems are made out of industrial proven material, a combination of ceramics and stainless steel. They are lubricated by high efficiency grease for optimum lifetime. The pumps are manufactured with the latest technology of CNC machines to provide the high level quality standard which the high tech users expect. The quality of each pump is controlled automatically by frequency analysis before leaving the factory. For minimum footprint the TURBOVAC SL pumps can be equipped with the box controller mounted on the pump body at multiple sites as well as separated from the pump. This allows the user to optimize the available space in the vacuum system. The new "anybus" interface concept offers the choice between RS232, 485, Ethernet, profibus or 24V type. The new family of TURBOVAC SL turbomolecular pumps has been designed to provide proven quality in combination with highest flexibility in installation and communication. This makes the pump family the best solution for the use in analytical instruments, research labs in universities and industry and industrial production, i.e. thin film coating application.

10:20am **EW-WeM2 New Advances in Raman Microscopy Instrumentation***,* ***M.H. Wall***, Thermo Fisher Scientific

Raman microscopy provides valuable and important information about the molecular composition of a material under investigation. This information is complementary to other recognized techniques for material analysis such as SEM and XPS and as such augments the information provided by these and other technologies. This presentation will highlight the recent advances in Raman micrsocopy instrumentation that have yielded instruments that are no longer instruments for only dedicated Raman researchers but are analytical tools that can also be effectively used by the non expert. Examples will also be presented that displays the applicability and importance of Raman microscopy in the field of materials characterization.

# Wednesday Lunch, October 22, 2008

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-WeL

## Exhibitor Workshops
**Moderator:** R.A. Childs, MIT

12:40pm **EW-WeL1 Characterization and Optimization of Polyatomic Ions for XPS Depth Profiling of Organic Materials**, ***C.J. Blomfield****, S.C. Page, D.J. Surman, S.J. Hutton, A.J. Roberts, S.J. Coultas*, Kratos Analytical Ltd, UK

X-ray Photoelectron Spectroscopy (XPS) depth profiling of inorganic materials has become a standard analytical technique. Results can be obtained relatively quickly with good interface resolution while maintaining chemical information. It has become desirable to achieve the same performance on organic materials however there are several well known problems associated with sputter depth profiling which has limited the application. In recent years there has been significant development in the TOF-SIMS community of the use is polyatomic ion sources and in particular C60 for the generation of molecular species from organic materials. This use of C60 has been extended to XPS depth profiling and for some materials has shown good promise. This paper discusses the characterization and optimization of other polyatomic species in addition to C60 that are also showing considerable promise for XPS depth profiling of organic materials.

1:00pm **EW-WeL2 State-Of-The-Art Software and Surface Analysis at Thermo Fisher Scientific**, *R.G. White,* ***P. Mack***, Thermo Fisher Scientific, UK

State-of-the-art XPS instruments require state-of-the-art software for system control and data processing. If the software is not easy to use whilst at the same time being powerful and flexible, then the high performance offered by the hardware may not be realised in everyday usage. Additionally, the increased sample throughput afforded by high sensitivity data acquisition can be compromised if time is then wasted during data processing or reporting. Thermo Scientific's Avantage software combines advanced XPS instrument control and data processing, creating an integrated workflow from data acquisition to data reporting. The high level of integration between instrument control and data processing offered by Avantage allows recipes to be created which automate both the acquisition and processing of XPS data. Avantage recipes can be programmed with the knowledge and experience of an expert user, allowing repetitive, but complex, tasks to be fully software controlled. Workflows with advanced data acquisition and peak fitting protocols, for example, can be created which automatically reduce vast XPS datasets to a set of pass-fail parameters. These expertly crafted recipes can be used by both novice and advanced users. Avantage features a wide variety of data processing tools which enable the user to move from raw XPS data to useful real-world parameters quickly and easily.

1:20pm **EW-WeL3 XPS Sputter Depth Profiling and Surface Cleaning with C60 Sputter Ion Beams**, ***J.F. Moulder****, S.N. Raman, J.S. Hammond*, Physical Electronics

C60 sputtering has emerged as a standard method for XPS depth profiling of polymer, organic, and biomaterial thin films. Several years of exploratory use of C60 ions for sputter cleaning and depth profiling has shown C60 sputter cleaning can be successfully applied to a very broad range of materials with good success and that C60 depth profiling, while not universally applicable, has been successfully used to study a number of important and commonly used materials systems. We will present an overview of our experience with C60 sputtering as it relates to XPS and highlight the strengths and limitations of this new surface characterization method. Experimental results from inorganic, polymer, and biomaterials will be presented to illustrate the application potential for XPS and C60 sputtering.

## Applied Surface Science
## Room: 207 - Session AS-WeA

## Frontiers of Analysis and Combined Materials
**Moderator:** D.J. Gaspar, Pacific Northwest National Laboratory

1:40pm **AS-WeA1 Ambient Surface Mass Spectrometry – DESI – Towards a Metrological Framework**, *F.M. Green,* National Physical Laboratory, UK*, P. Stokes, G. O'Connor,* LGC Ltd., UK*, **I.S. Gilmore***, National Physical Laboratory, UK **INVITED**

There has been an explosion in the growth of ambient surface mass spectrometries with new ionisation and desorption methods developing rapidly. Surface chemical analytical techniques such as SIMS are extremely powerful providing high-sensitivity molecular information at better than 200 nm spatial resolution. However, the requirement for analysis in vacuo is for many applications a severe drawback. This is, of course, particularly important in biology. In the vanguard of these ambient methods is Desorption Electrospray Surface Ionisation (DESI) developed by the Cooks group.[1,2] DESI has already been shown to have great potential in a wide range of application areas from forensics and homeland security, through to counterfeit detection of pharmaceuticals and biological analysis. Of the wide variety of desorption methods it is clear that DESI has one of the strongest uptakes and so it is with DESI that we begin the development of a metrological approach, similar to that developed for SIMS and XPS. The objective is to improve repeatability and reproducibility and consequently confidence in the method and uptake into industry. A first step in the development of a metrological framework is to measure and improve repeatability. Here we conduct a systematic study of the parameters affecting spectral intensities and the interaction of the electrospray jet with the material surface. We have developed a well-controlled model system of Rhodamine B on glass that allows the effect of key experimental parameters such as geometry and spray conditions to be studied and optimised. Using this approach we have improved the repeatability of spectral intensities to 20%. In addition, we have studied the surface crater and surrounding disrupted material which gives insights into the interaction mechanism of the electrospray jet and the surface. This is important to allow future improvements in resolution and to understand the rate at which material is removed.

[1] Z. Takats, J. Wiseman, B. Gologan, G. Cooks; Science, 306 (2004) 471

[2] G. Cooks, Z. Ouyang, Z. Takats, J. Wiseman, Science, 311 (2006) 1566.

2:20pm **AS-WeA3 Shallow-Depth Surface Etching by Electrospray Droplet Impact**, ***K. Hiraoka***, *Y. Sakai, D. Asakawa,* University of Yamanashi, Japan*, Y. Iijima*, JEOL Ltd.

A new ionization method, electrospray droplet impact (EDI) ionization, has been developed for matrix-free secondary ion mass spectrometry (SIMS).[1,2] The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure are sampled through an orifice with a diameter of 400 µm into the first vacuum chamber, transported into a quadrupole ion guide, and accelerated by 10kV after exiting the ion guide. The water droplets impact on a dry solid sample ( no matrix used) deposited on a stainless steel substrate. The secondary ions formed by the impact are transported to a second quadrupole ion guide and mass-analyzed by an orthogonal time-of-flight mass spectrometer (TOF-MS). EDI was applied to peptides, synthetic polymers, and inorganic materials. It was found that EDI/SIMS has a high sensitivity without damaging the sample underneath and the film thickness desorbed by a single collisional event is to be less than a few monolayers. An instant conversion (in subpicoseconds) of kinetic energy of the impinging water droplet to the internal energies of molecules in the colliding selvedge takes place, i.e., sample molecules in the shock-wave excited selvedge suffer from the electronic excitation leading to the desorption/ionization. In the EDI mass spectra for PET, several fragment ions were observed but the XPS spectra did not change with prolonged cluster irradiation. This indicates that the surface of PET was etched with little surface damage. In the EDI mass spectra for tin and silicon, the major secondary ions observed were protonated oxide ions such as $H^+(SnO)_n$ and $H^+(SiO_2)_n$. This suggests that the oxidative chemical etching takes place in the selvedge of the colliding interface resulting in the atomic-level surface etching. Acknowledgement: This work was supported by the Japan Science and Technology Agency

[1] K. Hiraoka, D. Asakawa, S. Fujimaki, A. Takamizawa, K. Mori, Eur. Phys. J. D 38 (2006) 225.

[2] K. Hiraoka, K. Mori, D. Asakawa, J. Mass Spectrom., 41 (2006) 894.

2:40pm **AS-WeA4 Application of TOF-SIMS and LEIS for the Characterization of Ultra-Thin Films**, ***T. Grehl***, *D. Rading, E. Niehuis,* ION-TOF GmbH, Germany*, R. ter Veen, H. Brongersma,* Calipso BV, The Netherlands*, M. Fartmann, B. Hagenhoff*, TASCON GmbH, Germany

The continuous scaling of semiconductor devices (film thickness, junction depth) to smaller dimensions increases the challenges for the established analytical methods. In addition, new and more complex materials are introduced into the devices. Secondary Ion Mass Spectrometry (SIMS) and more recently Time-of-Flight (TOF-) SIMS have become workhorses for the semiconductor industry. The depth distribution of implants as well as impurities is regularly monitored using Cs and $O_2$ sputter depth profiles. Meanwhile sputter energies as low as 200 eV are routinely used in order to achieve a high depth resolution. Even at these low sputter energies the transient effects prevent establishing a reliable depth scale and deriving quantitative information on the first few nm. In addition, concentrations exceed the dilute limit, thus further complicating the quantification process.In this situation, complementary techniques become increasingly important. One of the emerging techniques is Low Energy Ion Scattering (LEIS) using high sensitivity analyzers. It is extremely surface sensitive and provides quantitative information on the outermost atomic layer of a solid. Low energy (1 – 10 keV) noble gas ions (He, Ne, ...) are used as projectiles. The energy of the back-scattered ions from elastic collisions is characteristic for the masses of the target atoms and is measured using an electrostatic energy analyzer. Quantification is comparatively straightforward and bulk standards can be used to determine the sensitivity factors. In addition, information can be gained on the surface near depth distribution of elements (1 – 10 nm) by measuring the extra energy loss of ions scattered in deeper layers (non destructive, "static mode"). This can be combined with conventional sputter depth profiling using a separate beam of low energy noble gas ions ("dynamic mode").

In order to compare the performance of LEIS with TOF-SIMS results for the characterization of ultra-shallow layers we studied a variety of typical sample systems such as ultra-shallow As implants, high-k films, and diffusion barriers at different stages of ALD growth. The results are discussed with respect to information depth, ease of quantification and sensitivity. It can be shown that the static profiling approach of LEIS is extremely powerful in the first few nm of the profile whereas due to its higher sensitivity SIMS performs better after sputtering through the transient region.

3:00pm **AS-WeA5 Use of Ion-Solid Interaction Theory to Optimize FIB Processes**, ***L.A. Giannuzzi***, FEI Company

Focused ion beam (FIB) techniques have been used over the years to prepare specimens for characterization in a wide range of analytical instruments. One of the more popular uses of FIB is for the production of transmission electron microscopy (TEM) specimens. The advent of FIB for the preparation of specimens for 3D atom probe tomography (APT) allows for analysis of multi-phased and multi-layered materials which in the past would have been considered difficult or impossible due to specimen preparation constraints. In addition, FIB prepared surfaces are now routinely used for the acquisition of electron backscatter diffraction (EBSD) patterns. This technique has been extended to the acquisition of 3D crystallography in a DualBeam (FIB+SEM) instrument. Typical FIB instruments operating at 30 keV can result in sufficient lateral ion implantation and/or amorphization surface damage to hinder quantitative high resolution TEM results. Amorphization damage can also degrade the quality of the EBSD pattern such that the pattern cannot be resolved. In addition, 30 keV FIB milling can cause sufficient ion mixing which can destroy the chemical/elemental integrity of interfaces, rendering the 3D APT analysis useless. New advances in ion columns allow for imaging and FIB milling to take place down to 500 eV. Specimens can be prepared using the fine probe size of the high energy beam, and then polished with low energy ions which replace the high energy implantation damage with minimal damage from the lower energy ions. These low energy FIB techniques allow for quantitative high resolution (S)TEM, improve the quality of the EBSD patterns, and allow for 3D APT without interferences from the Ga+ ion implantation. In addition, since materials exhibit different collision cascade characteristics as a function of incidence angle, prototyping can be optimized by controlling the incidence angle and scan direction of the ion beam which can influence the profile and aspect ratio of the milled region.

### 4:00pm **AS-WeA8 C60 Bombardment of Si - New Insights from SIMS and TEM**, ***G. Gillen**, C. Szakal, A. Herzing, I. Anderson,* National Institute of Standards and Technology*, S. Hues,* Micron Technology*, J. Bennett*, Process Characterization Laboratories, ATDF

There is continued interest in the development of novel cluster primary ion beams for applications in Secondary Ion Mass Spectrometry (SIMS). A C60 primary ion incident on a silicon substrate with an impact energy of 3000 eV would dissociate into 60 carbon atoms, each with an impact energy of only 50 eV. Since the depth resolution of a SIMS depth profile is directly related to the primary projectile energy, the use of such a cluster ion provides a possible method for obtaining ultra-high resolution SIMS depth profiles. Based on our previous experience with depth profiling of semiconductor materials using smaller cluster beams, it was hoped that C60 cluster SIMS would provide large improvements in depth resolution over conventional SIMS. Unexpectedly, initial evaluation of C60 SIMS depth profiling using delta-doped test samples demonstrated that deposition of an amorphous carbon layer on the silicon substrate was common, limiting the utility of C60 for depth profiling at impact energies below ~12 keV. Higher bombardment energies can minimize deposition but substantial degradation in depth resolution is observed compared to conventional SIMS depth profiling. This degradation was initially thought to result only from the formation of surface topography. In this work we have investigated the nature of the altered layer produced by C60 bombardment of silicon using SIMS and cross sectional transmission electron microscopy (TEM). Surprisingly, TEM imaging suggests the depth of penetration of carbon into the silicon substrate is substantially greater than would be predicted by simple ion implantation models. Furthermore, the buried interface between crystalline silicon and the carbon-rich altered layer exhibits nm scale roughness. These observations may help to explain the degradation in depth resolution commonly observed in C60 depth profiling of silicon materials. The enhanced diffusion of carbon beyond the penetration depth of the C60 may by explained by the enhanced diffusion of carbon in silicon resulting from strain produced in the silicon by high dose carbon implantation.

### 4:20pm **AS-WeA9 Understanding the Relationship between Chemical Vapor Deposition Precursor Structure and Film Properties by Application of Electron, Optical, Ion, and X-ray Characterization Methods**, ***B.W. Schmidt**, B.R. Rogers, R.D. Geil*, Vanderbilt University

Ceramic oxides such as $Al_2O_3$ and $HfO_2$ are desirable in microelectronics as high-κ replacements of $SiO_2$ and in high temperature applications as protectants. For multi-component systems like CMOS devices and thermal barrier coatings, characterization and control of bulk and interfacial properties are important for optimal performance. Chemical vapor deposition (CVD) is popular for its high deposition rates and good conformality. However, final properties of a CVD film can be greatly influenced by the choice of precursor. Novel precursor ligand designs are used to increase volatility and precursor throughput, but can also affect film composition, microstructure, and the deposition window. In this study, ligand effects are investigated by understanding the deposition processes of dimethylaluminum isopropoxide (DMAI) and methylaluminum di-isopropoxide (MADI). These are derivatives of popular precursors trimethylaluminum (TMA) and aluminum tri-isopropoxide (AIP). TMA is well-suited for CVD bubbler delivery systems due to its high vapor pressure and liquid state at room temperature, but is dangerous to handle and requires an oxidant source. AIP has the advantage of being a single-source precursor for $Al_2O_3$, but requires melting at 130°C to achieve consistent precursor flux. DMAI and MADI represent one and two methyl-isopropoxide substitutions of TMA, respectively. A goal is to achieve a single precursor with beneficial characteristics of TMA and AIP. Film characterization by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), spectroscopic ellipsometry, and medium energy backscattering spectrometry provide insight into initial stage and bulk deposition. Correlation of composition, microstructure, and chemical state progression to deposition conditions will aid in the development of application-specific precursors.

### 4:40pm **AS-WeA10 The Interface Formation between Calcium and Poly(3-hexylthiophene) Investigated with Adsorption Microcalorimetry, High-Resolution XPS and ISS**, ***F. Bebensee***, Universitaet Erlangen, Germany*, J.F. Zhu,* University of Science and Technology of China*, J.H. Baricuatro, J.A. Farmer, W. Lew,* University of Washington*, H.-P. Steinrueck, J.M. Gottfried,* Universitaet Erlangen, Germany*, C.T. Campbell*, University of Washington

Regioregular poly(3-hexylthiophene) (rr-P3HT), a semiconducting polymer, is widely used in organic electronics (OLED, OFET). Both the interface structure and the interaction strength between the polymer and the electrode (e.g. Ca) are very important for the performance of such devices. The heat of adsorption, which directly reflects the bonding energy between the metal and the polymer, was probed using adsorption microcalorimetry. We find high initial heats of adsorption indicating a strong interaction between Ca and rr-P3HT. In high-resolution X-ray photoelectron spectroscopy (XPS) experiments, a substantial shift of the S 2p signal suggests electron transfer from Ca to S in the polymer. We therefore conclude that the high initial heat of adsorption is due to the interaction of Ca atoms with S in the sample. Furthermore, shifts of the C 1s signal imply a band bending of about 0.5 eV, while no hints for structural degradation of the polymer can be found. Ion scattering spectroscopy (ISS) measurements suggests that the initial Ca reacts below the surface, followed by 3D Ca island growth. Both of these observations are corroborated by the XPS measurements. We also investigated the effects of electron irradiation of the polymer surface prior to Ca evaporation. Financial support by the DAAD and the NSF is gratefully acknowledged.

### 5:00pm **AS-WeA11 Synthesis and Characterization of Core/Shell Nanoparticle Thin Films for Gas Analytical Microdevices**, ***M. Bruns**, M. Fuchs, R. Ochs, S. Schlabach, D.V. Szabó,* Forschungszentrum Karlsruhe GmbH, Germany*, T. Grehl, S. Kayser,* ION-TOF GmbH, Germany*, M. Fartmann*, Tascon GmbH, Germany

Sputtered $SnO_2$ thin films are well established as gas sensing layers in analytical micro systems such as the Karlsruhe micro nose (KAMINA). To improve the performance towards higher sensitivity a very promising approach is to replace the sputtered thin films with films made of $SnO_2$ nanoparticles. This can easily be achieved by the Karlsruhe microwave plasma process (KMPP), a versatile precursor based gas-phase plasma process suited to synthesize nanoscaled particles with diameters less than 5 nm.[1] Regarding long-term stability, such $SnO_2$ nanoparticles can be coated in-situ with a protective ultra-thin $SiO_2$ shell in a downstream step and then directly deposited onto the respective micro devices. These core/shell nanoparticles are expected to prevent the gas sensitive core from growing and agglomeration, respectively, while preserving electrical contact. The prerequisite is to achieve an inhomogeneous $SiO_2$ shell enabling direct contact between adjacent $SnO_2$ nanoparticles, i.e. simply acting as a spacer.

This contribution focuses on the characterization of nanoparticle thin films with a thickness of 200 nm made of core/shell $SnO_2$/ $SiO_2$ nanoparticles by means of X-ray photoelectron spectroscopy (XPS). The main points of interest in this context are chemical binding states and information on the shell thickness in a non-destructive manner. For this purpose, the $SiO_2$ shell thickness systematically was increased while keeping the $SnO_2$ core size constant. In case of the desired inhomogeneous ultra-thin $SiO_2$ shells low energy ion scattering (LEIS) solely is a suitable means to distinguish between Sn and Si within the outermost monolayer of the spherical particles to prove the attainability of open-pored coatings. In addition, transmission electron microscopy (TEM), X-ray diffraction (XRD), and He-Pycnometry were used to achieve a comprehensive characterization.

[1] B. Schumacher, R Ochs, H. Troesse, S. Schlabach, M. Bruns, D. V. Szabó, J. Haußelt, Plasma Process. Polym. 4 (2007) 865.

### 5:20pm **AS-WeA12 Molecular Depth Profiling for Soft Materials by using Size-Selected Large Cluster Ions**, ***J. Matsuo**, S. Ninomiya, H. Yamada, K. Ichiki, Y. Nakata, T. Aoki, T. Seki*, Kyoto University, Japan

Interest in soft materials, such as polymers or biological materials, has increased in the last decade. SIMS analysis and molecular depth profiling of soft materials with polyatomic and cluster ions have been demonstrated recently. The multiple collisions and high-density energy deposition of these ions on solid surfaces induce enhancement of sputtering and secondary ion yields, as well reduced residual surface damage compared with other techniques. We have demonstrated that the sputtering yields of polymer and amino acids with large Ar cluster ions (mean size: 1000) at the energy of 20 keV are more than 100 molecules/ion, and sputtered surfaces are much smoother than the original surfaces. Secondary ions emitted from arginine (Arg, C6H14N4O2), leucine (Leu, C6H13NO2), glycylglycylglycine (GlyGlyGly, C6H11N3O4), polymethyl methacrylate (PMMA), and tris (8-hydroxyquinoline) aluminum (Alq3, C27H18AlN3O3) films were measured using the time-of-flight (TOF) technique under the incidence of large Ar cluster ions at incident energies of 3 and 20 keV. The ratio of fragment ions to molecular ions decreases quite rapidly with increasing cluster size. Very few fragment ions were observed in the mass spectrum, when the cluster size was larger than 1000. The kinetic energy of a few eV/atom is comparable to the bonding energy of molecules. We have found that residual damage is strongly dependent on the incident velocity of cluster ions, when the size of the cluster ion is larger than 100, and this result is well matched with recent MD simulations. Ultra-low energy SIMS and molecular depth profiling of various soft materials can be realized by using large Ar cluster ions. Recently, molecular depth profiling with low energy (<500eV) monomer ions has also been reported for various polymers. However, in order to realize molecular depth profiling the primary monomer ion beam has to be carefully chosen. The atomistic mechanism of energetic large cluster impacts and the prospects of this technique will be discussed in conjunction with the size effect in secondary ion emission and damage cross-section.

## Biomaterial Interfaces
## Room: 202 - Session BI-WeA

### Quantitative Analysis of Biointerfaces
**Moderator:** D.G. Castner, University of Washington NESAC/BIO

1:40pm **BI-WeA1 'Structure' of Water: Myth or Reality?**, ***M. Grunze***, University of Heidelberg, Germany **INVITED**

The "structure" of water at interfaces is a reoccurring interpretation of experimental data or computer simulations employing simplified models for liquid water. Oriented binding of water molecules to a hydrogen bridge bond donor or acceptor group, as observed e.g. in vibrational spectroscopies, does not imply translational symmetry or "structure", and the orientational order parameter decays typically with the second hydration shell. Whereas the practical significance of surface energy and hence wetability of organic surfaces for adhesion, adhesion failure and biomolecule interaction is obvious, the molecular basis of the hydrophobic and hydrophilic properties of organic surfaces is poorly understood. This is due to the lack of suitable experimental tools for detailed spectroscopy studies of organic interfaces in liquid environments and of molecular detailed theoretical descriptions of hydrophobic/hydrophilic interactions. In this talk I will briefly discuss the limits and potentials of experimental approaches to interfacial water (Neutron Reflectivity, Sum Frequency Generation Spectroscopy, and Terahertz Spectroscopy) to develop a molecular understanding of the properties of water in organic interphases of different surface energy; and time permitting get back to a long standing controversy, the "inert" surface problem, which is a good example for demonstrating the complexity of interfacial water properties.

2:20pm **BI-WeA3 A Novel Approach to XPS Characterisation of 'Click' Surface Chemistry, More Information Less Damage**, ***T.S. Nunney***, *R.G. White,* Thermo Fisher Scientific, UK, *N.B. Larsen, T.S. Hansen, A.E. Daugaard, S. Hvilsted*, Technical University of Denmark

'Click' chemistry is increasingly used for chemical surface engineering of polymer devices to be used in biological and medical applications. Advantages of 'click' chemistry include mild reaction conditions, i.e. aqueous environment at room temperature, and high chemical specificity of the coupling. We recently demonstrated surface engineering of ultrathin electrically conductive polymer films by 'clicking' organic functional units that control wettability, protein adhesion, or fluorescence, all functions of major relevance to biomedical applications. The most commonly used click reaction is based on the coupling of organic azides to alkynes. This is also the basis of our recently reported functional monomer, azide modified 3,4-ethylenedioxythiophene, for conducting polymer films (PEDOT-N3) reactive towards alkyne functionalized molecular species. The ability of X-ray photoelectron spectroscopy (XPS) to provide quantitative chemical state information makes it ideal for the investigation of the resultant clicked surface chemistry. In the example above, differences in the XPS binding energy for the azide and triazole nitrogens serve as a useful method to determine if the click reaction has completed successfully. It is known, however, that degradation of the azide chemistry during XPS measurement process can significantly obscure the result. In this paper we will discuss methods for minimisation of the measurement-induced chemical degradation. These methods rely on a number of hardware and software features which have recently become available on modern XPS instrumentation. The methods described require the layers to be uniform so that the data can be collected as a map, thus reducing the X-ray and electron flux density during the measurement. Deconvolution routines will be shown to facilitate the rapid chemical state mapping of patterned variants of these surfaces.

2:40pm **BI-WeA4 A New QCM-D and Reflectometry Instrument - Applications to Supported Lipid Structures and their Interactions**, ***M. Edvardsson***, *S. Svedhem,* Chalmers University of Technology, Sweden, *G. Wang,* Chalmers University of Technology and Q-Sense AB, Sweden, *R. Richter,* CIC biomaGUNE, Spain, *M. Rodahl,* Q-Sense AB, Sweden, *B. Kasemo*, Chalmers University of Technology, Sweden

In the past decade, the Quartz Crystal Microbalance with Dissipation monitoring technique (QCM-D) has emerged as a powerful biosensor technique.[1] A key feature of the technique is that the shift of the resonant frequency, $\Delta f$, obtained upon adsorption of mass on the QCM-D sensor surface includes both the actual mass and solvent (e.g. water) associated with it. For a rigid film containing no water (low dissipation shifts, $\Delta D$), the frequency shift, $\Delta f$, can be considered proportional to the mass of the film. For viscoelastic films containing water (high dissipation shifts), however, it is difficult to determine how much of the frequency shift results from the actual adsorbed mass and how much is a contribution from entrapped or associated water. In some applications, the signal enhancement that is obtained through the associated liquid, makes the QCM-D technique unique with respect to the added information that is gained compared to, for example, optical techniques. In particular, spontaneous fusion of lipid vesicles onto solid supports have been studied extensively using the QCM-D technique,[2] and unique new information has been obtained. However, for a full picture one would, for such complex viscoelastic films, ideally combine the QCM-D technique with a technique that allows separation of the adsorbed (non-hydrated or "dry") mass and the associated liquid (wet mass). This presentation demonstrates applications of a recently developed instrument, combining, on the same sensor surface, the QCM-D technique and optical reflectometry [Wang et al., submitted to Rev. Sci Instr,], for surface based analysis of biomolecular and polymer adlayers. The combination instrument makes it possible to do simultaneous, time-resolved measurements of hydrated and non-hydrated mass and viscoelastic properties of films and molecular adlayers formed on the surface. The experimental setup is described, and the value of this combination of techniques is demonstrated via applications on model systems that involve supported lipid structures of various degree of hydration; ranging from systems of low water content, e.g., bilayers, to those of high water content, such as surface-attached vesicles and bilayers with a highly hydrated peptide coupled to it.

[1] Cooper, M. A.; Singleton, V. T. J. Mol. Rec. 2007, 20, 154-184.

[2] Richter, R. P.; Bérat, R.; Brisson, A. Langmuir 2006, 22, 3497-3505.

3:00pm **BI-WeA5 Calculation of Adsorption Free Energy for Peptide-Surface Interactions using Molecular Dynamics Simulation Methods**, ***N. Vellore***, *S.J. Stuart,* Clemson University, *B.R. Brooks,* National Institutes of Health, *R.A. Latour*, Clemson University

While it is well understood that protein-surface interactions are of fundamental importance for understanding cell-surface interactions, very little is understood at this time regarding the molecular level events that control protein adsorption behavior. Molecular dynamics simulations methods have enormous potential for development as a tool to help understand and predict protein adsorption behavior. These methods, however, must first be developed and validated for this specific application. One of the most important areas for development is the assessment and validation of force field parameters that will enable the competition between amino acid residues of a peptide or protein and molecules of the solvent (i.e, water and salt ions) for the functional groups presented by a surface. One of the fundamental driving forces that control these types of interactions is the free energy of adsorption. We have therefore developed a method of accurately calculating the adsorption free energy of peptide-surface interactions using molecular dynamics simulations with an advanced sampling algorithm called biased replica-exchange molecular dynamics (biased-REMD). Simulations are performed with the CHARMM force field and simulation package using explicitly represented solvent (150 mM Na+/Cl- in TIP3P water) with periodic boundary conditions. A host-guest peptide model is used for these simulations in the form of TGTG-X-GTGT, where the T (threonine) and G (glycine) flanking sequences are the host residues and X represents a variable guest residue. Alkanethiol self-assembled monolayers (SAMs) with a broad range of polymer-like functionalities are being used as the adsorbent surfaces. The results of these simulations are being compared with complementary experimental studies using these same peptide-SAM systems in order to evaluate the accuracy of the force field, and to provide a basis for force field parameter modification for the development of a validated force field parameter set for the accurate representation of peptide-surface interactions. Once developed, these methods will be able to be applied to accurately simulate protein-surface interactions, thus providing a valuable resource to investigate protein-surface interactions at the molecular level.

4:00pm **BI-WeA8 Nonlinear Light Scattering: Bridging the Gap between Surface Science & Soft Matter**, ***S. Roke***, Max-Planck Institute for Metals Research, Germany **INVITED**

Interfaces play a key role in many processes. They play a regulating role in transport and structural phenomena in biological cells, they can determine the chemistry and (phase) behavior of colloidal systems, they are important for the mechanical properties of (amorphous) solids and they determine the electrical properties of micro- and nano-electronics. When the size of materials decreases down to the level of micro- or nano-structures, the relative interfacial area increases. For small systems it is well-known that the interfacial region becomes a dominating factor in determining the physical and chemical properties of a material. Thermodynamically, on a macroscopic level, the effect of an interface region is well understood. On a molecular level, however, it is not. In this presentation I will introduce vibrational sum frequency scattering as a novel method to investigate particle and domain interfaces,[1] highlight new possibilities that become available and show some of the latest developments. These include: the possibility of investigating molecular surface effects in colloidal phase transitions,[2,3] how to extract molecular properties[4] and the possibility of observing embedded domain structures in polymorph materials.[5]

[1] - S. Roke, W. G. Roeterdink, J. E. G. J. Wijnhoven, A. V. Petukhov, A. W. Kleyn and M. Bonn, Phys. Rev. Lett., 91 (2003), 258302-1.

[2] - S. Roke, J. Buitenhuis, M. Bonn and A. Van Blaaderen, J. Phys.: Condens. Matter., 17 (2005), S3469-S3475.

[3] - S. Roke, J. Buitenhuis, A. van Blaaderen and M. Bonn, Proc. Nat. Acad. Sci, 103 (2006), 13310-13314.

[4] - A. G. F. de Beer and S. Roke, Phys. Rev. B, 75 (2007), 245438-1-8.

[5] - A. G. F. de Beer, H. B. de Aguiar, J. F. W. Nijsen, A. B. Sugiharto and S. Roke, submitted.

4:40pm **BI-WeA10 Characterization of DNA Monolayers on Gold using Sum Frequency Generation Spectroscopy**, ***C.L. Howell***, *M. Grunze, P. Koelsch*, University of Heidelberg, Germany

We investigated a series of model monolayers of single stranded DNA (ssDNA) on gold using broadband femtosecond Sum Frequency Generation (SFG) Spectroscopy. SFG processes, involving a non-linear resonant responses produced by exciting vibrational modes of molecular bonds using overlapping IR and visible beams, are inherently interface-specific. The surface specificity of SFG, combined with polarization dependence, allows for the investigation of the ordering and orientation of molecules at surfaces in air and through bulk solutions. However, due to the difficulties associated with operating an SFG system in biological relevant spectral regions (such as the amide I and fingerprint), combined with the difficulties of interpreting vibrational spectra from complex biomacromolecules, there are few published examples of characterization of DNA films using SFG. Our goal is to create high quality vibrational SFG spectra of model monolayers of DNA on gold and to compare these spectra to results obtained from complementary surface spectroscopies that have been applied to DNA monolayers, such as XPS, FTIR, and NEXAFS. Preliminary results in the C-H stretching region show distinctive changes in the locations and relative intensities of peaks for a film of thiol-modified 5-mers of thymine (T5-SH) compared to thiol modified 25-mers (T25-SH) and unmodified thymine 5-mers (T5). Preliminary SFG spectra of ssDNA films in the Amide I region revealed changes in the locations and intensities of the major peaks for the T5 film compared to a film of unmodified adenine 5-mers, as well as compared to T5-SH and T25-SH films. Refinement and validation of SFG Spectroscopy as a tool for the characterization of DNA monolayers on gold could provide another method for examining the structure of these films, and potentially serve as a bridge for comparing these systems ex situ and in situ.

5:00pm **BI-WeA11 Avoiding Parasitic Reactions Due to Interconnect Dead Volume and Non-Specific Binding in Microfluidics**, *X. Luo*, ***D.L. Berlin***, *W.E. Bentley, G.F. Payne, R. Ghodssi, G.W. Rubloff*, University of Maryland

Biological microelectromechanical systems (bioMEMS) provide an attractive approach to understanding and modifying enzymatic pathways by separating and interrogating individual reaction steps at localized sites in a microfluidic network. We have previously shown that electrodeposited chitosan enables immobilization of an enzyme at a specific site while maintaining its catalytic activity. While promising as a methodology to replicate metabolic pathways and search for inhibitors as drug candidates, these investigations also revealed unintended (or parasitic) effects, including products generated by the enzyme either (1) in the homogeneous phase (in the liquid), or (2) nonspecifically bound to microchannel surfaces. Here we report on bioMEMS designs that significantly suppress these parasitic effects. To reduce homogeneous reactions we have developed a new packaging and assembly strategy that eliminates fluid reservoirs that are commonly used for fluidic interconnects with external tubing. To suppress reactions by nonspecifically bound enzyme on microchannel walls we have implemented a cross-flow microfluidic network design so that enzyme flow for assembly and substrate/product flow for reaction share only the region where the enzyme is immobilized at the intended reaction site. Our results show that the signal-to-background ratio of sequential enzymatic reactions increases from 0.72 to 1.28 by eliminating the packaging reservoirs, and increases to 2.43 by separating the flow direction of enzymatic reaction from that of enzyme assembly. These techniques can be easily applied to versatile microfluidic devices to minimize parasitic reactions in sequential biochemical reactions.

5:20pm **BI-WeA12 Probing Orientation and Conformation of α-Helix and β-Sheet Model Peptides on Self-Assembled Monolayers with SFG and NEXAFS Spectroscopy**, ***T. Weidner***, *J. Apte, L.J. Gamble, D.G. Castner*, University of Washington

Understanding the interaction of proteins and peptides with engineered surfaces from first principles is essential for the design of biomaterials which are applicable in antifouling, implant technology and immunosensors. Controlled immobilization of peptides onto artificial biointerfaces plays a key role in these technologies and it is of crucial importance to develop tools to examine interfacial properties of adsorbed peptides such as orientation, and secondary structure. In this study we used sum frequency generation (SFG) vibrational spectroscopy and near edge X-ray absorption fine structure (NEXAFS) spectroscopy to characterize the structure of α-helix and β-strand model peptides on self-assembled monolayers (SAMs). The formation of peptide monolayers was confirmed using X-ray photoelectron spectroscopy. The α-helix peptide is a 14-mer and the β-strand is a 15-mer of hydrophilic lysine (K) and hydrophobic leucine (L) residues with a hydrophobic periodicity of 3.5 and 2, respectively. Both peptides have the hydrophobic side-chains on one side and the hydrophilic on the other. The SAMs used as hydrophobic and hydrophilic model surfaces were prepared from alkane thiols on gold having either charged COOH or hydrophobic $CH_3$ units as terminal groups. For SFG studies we used the deuterated analog of the latter SAM. SFG spectra collected in the C-H region exhibit strong peaks near 2965 cm$^{-1}$, 2940 cm$^{-1}$ and 2875 cm$^{-1}$ related to ordered leucine side chains on both surface chemistries. The relative phase of these features revealed the orientation of the leucine side chains. On COOH a relative phase of 1.4 and 1.6 rad for α-helix and β-strand, respectively, showed that the leucine was oriented away from the surface while a phase of 0 rad for both peptides on $CH_3$ proved that the leucines are oriented towards the interface. Amide I peaks observed at 1656 cm$^{-1}$ for the α-helix peptide confirm that the secondary structure is preserved on both SAMs. A strong linear dichroism related to the amide $\pi^*$ orbital at 400.1 eV was observed in the nitrogen K-edge NEXAFS spectra for the β-strand peptides on both surfaces, suggesting that the peptides are oriented parallel to the surface with the side-chains normal to the interface. For the α-helix the dichroism of the amide $\pi^*$ is weak, probably due to the broad distribution of amide bond orientations for this secondary structure.

## 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 $CaF_2$ 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 $CaF_2$, 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 tetracylcine 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.

[1] M. Zhou, C. Wu, A. Akhmetov, P.D. Edirisinghe, J.L. Drummond and L. Hanley, J. Amer. Soc. Mass Spectrom. 18, 1097 (2007).

[2] G.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-fractioning 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 $-CH_3$ 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 $-COOH/-CH_3$ 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 $-COOH/-CH_3$ 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 $TiO_2$**, ***P. Sjovall***, 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 $TiO_2$ 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 $Bi_3^+$ 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]

[1] Prinz 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 (100µm). 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.

[1] Brunelle,A,et al. Journal of Mass Spectrometry 2005,40,985-999

[2] Fletcher,JS,et al. Analytical Chemistry 2006,78,1827-31

[3] Azrak,RG,et al. Biochemical Pharmacology 2007,73,1280-1287

[4] Prieto Conaway,MC,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, $C_5H_8O_2$), and osmium tetroxide ($OsO_4$), respectively, were compared to a non-fixing protocol where cells were washed with ammonium formate (AF, $NH_4HCOO$) 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 $Bi_3$ 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 $OsO_4$ 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 $OsO_4$, than for GA fixed cells. An increase in amino acid intensity going from AF to GA to $OsO_4$ was also observed.

## Electronic Materials and Processing Room: 210 - Session EM+NC-WeA

## Molecular and Organic Electronics

**Moderator:** L.M. Porter, Carnegie Mellon University

1:40pm **EM+NC-WeA1 Metal-Molecule-Semiconductor Devices: Accurate Extraction of Device Parameters from Transport Measurements**, ***A. Scott***, *D. Janes*, Purdue University

In recent years there has been considerable interest in integrating molecular components into solid-state electronic devices for high-density memory, nanoelectronic, and sensing applications. Molecular devices directly grafted to semiconductors are of particular interest due to the electrically tunable nature and technological relevance of the substrates. Considerable experimental efforts have been invested in the fabrication and electrical characterization of metal-molecule-semiconductor (MMS) devices. When moderately-doped semiconductors are used in MMS structures, the devices exhibit Schottky diode-like behavior. Typically, current-voltage or capacitance-voltage characteristics of the devices are measured at room temperature and the results are analyzed by using well-known ideal Schottky diode relationships.[1] The Schottky barrier height, $\Phi_B$, is experimentally determined assuming that the electronic and structural properties of the interfaced are not significantly modified by the presence of the molecular layer. Although this approach has been used to offer valuable qualitative insights about effects such as the influence molecular dipole on $\Phi_B$,[2] it does not consider the detailed structural and electronic properties of the interface. Additional experimental and theoretical tools are needed to capture the interfacial physics introduced by the molecular electronic structure as well as non-idealities which are present at such hybrid interfaces. We present a MMS device model which considers the molecular electronic structure, semiconductor interface states, junction non-uniformity, and other important physical phenomena which are not present in the ideal Schottky diode model. The influence of various effects on current-voltage and capacitance-voltage characteristics are illustrated. Theoretical and experimental evidence is presented to show that temperature dependent transport allows for more accurate extraction of device parameters with fewer assumptions. The improved description MMS devices will shed additional light on the transport mechanisms that dominate these structures as the substrate and molecular properties are varied, leading to improved device design and characterization.

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2:00pm **EM+NC-WeA2 Silicon-on-Insulator based sub 10 nm Spaced Metal Electrodes for Hybrid Molecular Electronics**, *S. Strobel*, Technische Universität München, Germany, *R. Sondergaard*, Technical University of Denmark, *R. Murcia Hernandez*, Technische Universität München, Germany, *A. Hansen, F. Krebs*, Technical University of Denmark, *P. Lugli*, Technische Universität München, Germany, ***M. Tornow***, Technische Universität Braunschweig, Germany

In future microelectronic circuits a partial replacement of certain electronic functions by organic molecule junctions may become feasible. For such “hybrid” integration the fabrication of nanoscale contacts on the same semiconductor wafer using existing microelectronic process technology, only, will be advantageous. We investigated the fabrication of nanogap electrode devices based on silicon-on-insulator, by using optical lithography, a combination of dry and wet etching techniques and thin-film metal deposition. The prepared, smooth metallic contact pairs are separated by predetermined distances down to below 10 nm, and feature a well tailored material layer structure, as characterized by cross-sectional scanning TEM analysis. We studied the electronic transport properties of molecular wires based on conjugated organic molecules and molecule-nanoparticle hybrid systems. In the case of approx. 12 nm long dithiolated, oligo-phenylene-vinylene derivatives we observed a pronounced non-linear current-voltage characteristic at 4.2 K. The electronic states of the molecule have been studied by Density Functional Theory (DFT) in order to show the effect of the ligands and of the gold contacts. By using the results of the DFT calculations in a Non Equilibrium Green Function model, the current-voltage characteristics of OPVs have been analyzed, showing a good agreement with the experimental data. Low temperature transport through 30 nm gold nanoparticles positioned onto electrodes coated by a self-assembled monolayer of mercaptohexanol features a distinct Coulomb staircase behavior. These measurements are in excellent agreement with classical Coulomb blockade theory for an asymmetric double barrier tunneling system.

### 2:20pm **EM+NC-WeA3 Single Molecule Electronics and Sensors*, N.J. Tao***, Arizona State University **INVITED**

The ability to measure and control current through a single molecule is a basic requirement towards the ultimate goal of building an electronic device using single molecules. It also allows one to read the chemical and biological information of the molecule electronically, which opens the door to chemical and biological sensor applications based on electrical measurement of individually wired molecules. To reliably measure the current, one must: 1) provide a reproducible contact between the molecule and two probing electrodes; 2) find a signature to identify that the measured conductance is due to not only the sample molecules but also a single sample molecule; 3) provide a third gate electrode to control the current; and 4) carry out the measurement in aqueous solutions for biologically relevant molecules in order to preserve their native conformations. We will describe methods to attach a single molecule to two electrodes via covalent bonds and control the current through the molecule with an electrochemical gate, and report on sensor applications of the molecular junctions. We will also discuss unresolved issues in the attempt to measure and control electron transport in single molecules.

### 3:00pm **EM+NC-WeA5 Spectroscopic Observation of Conductance Switching with Inelastic Electron Tunneling Spectroscopy*, B.G. Willis***, University of Delaware

Molecular electronics is a promising area of research for creating electronic devices that can be integrated with semiconductor based nanoelectronics for novel capabilities such as molecular sensors. Recent literature data has shown that the electrical transport properties of molecules can be tuned through chemistry, and the long term expectation is that useful devices can be engineered through a combination of chemistry and electrical transport properties. It is also known that the electrical contact between a molecule and an electrode has a significant influence on electrical transport measurements, and these contact effects complicate the interpretation and design of molecular electronics devices. The contact effects become increasingly important as the number of molecules in the molecular transport junction is reduced toward the limit of a single molecule, and there is an urgent need to investigate contact effects in transport measurements. This is difficult due to the inherent nanoscopic nature of the experiments and the general lack of appropriate experimental tools. In this paper, we present an approach using inelastic electron tunneling spectroscopy (IETS) to investigate the chemistry and chemical bonding in electrode-molecule-electrode tunnel junctions. We present IETS spectroscopic observation of conductance switching for carbon monoxide bonded to a Cu/Pd bimetallic surface in a nanoelectrode junction. It is shown that the conductance switching is caused by the formation of an adatom on the surface that leads to an abrupt increase in the current of almost an order of magnitude. The new bonding arrangement leads to intense IETS features including the metal-CO bond stretch that has not previously been observed in related scanning tunneling microscopy IETS experiments. This work demonstrates that conductance changes in molecular electronics junctions can be studied and understood using IETS as a spectroscopic probe of the chemistry and bonding in the junction. Furthermore, it is shown that small molecules such as CO may be useful for characterizing electrode structure in molecular electronics measurements.

### 4:00pm **EM+NC-WeA8 Nanocontacts Inducing Surface Initiated Polymerization of Nanowires on Molybdenum Carbide*, I. Temprano***, Université Laval, Canada

The ability to develop new methods to enhance electrical contact between organic molecules and electrodes is fundamental to the design of devices that require electron flow between an organic and a metallic component. Metal-organic contacts using double and triple bonds is a promising approach in that it combines three advantages. First it offers a transmission coeficient not yet seen way ahead of any other molecular linkages yet known,[1,2] second they have enhanced thermal stability[3,9-10] over 900 K, and they show activity for olefin-metathesis add-on chemistry.[1] The dissociative adsorption of carbonyl compounds leads to the formation of C=Mo double bonds on the surface of molybdenum carbide.[3-6] These metal alkylidenes are mimics of well defined homogeneous metathesis catalysts, and present similar activity face to transalkylidenation and ring-opening polymerization (ROMP)[8] reaction. The data presented will show this breaktrhough catalytic system and its performance, paying especial attention to the formation and characterization of surface initiated metathesis polymerization of polyacetylene,[9] the simplest of the conjugated polymers, and an ideal candidate to study the special properties this system can developpe. This study opens a whole new era in which a very controllable reaction as olefin-metathesis may be used to grow technologically very interesting conjugated polymers, directly from a metallic surface, and hence, to interconnect electrodes, as nanowires, in nanodevices with great control and precission. Self-assembly of conjugated polymers may allow their targeted insertion into electronic and electrooptical devices.

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### 4:20pm **EM+NC-WeA9 Spatially Resolved Conductance Measurements of Novel Porphyrin-Chromophore Molecular Assemblies*, S.U. Nanayakkara*, *L. Kraya***, University of Pennsylvania*, T.-H. Park, J.T. Stecher, M.J. Therien,* Duke University*, D.A. Bonnell*, University of Pennsylvania

We have measured charge transport in individual porphyrin-chromophore molecules using an ultra-high vacuum scanning tunneling microscope. This class of fully conjugated molecules can include a mono- or multi-chromophoric center and a linker-group that terminates with a thiol or dithioate functionality. These functionalities facilitate attachment to a gold substrate. Therefore, in order to isolate individual and small groups of molecules we have utilized self- and directed-assembly using alkanethiolate self-assembled monolayers (SAMs) on Au(111). The alkanethiolate SAMs provide a support matrix confining the porphyrin-chromophore molecules into precise assemblies for charge transport measurements. We have further coupled a laser to the tunneling junction in order to record photo-induced single molecule charge transport measurements. We aim to understand the conductance pathways of these molecules with and without illumination, and as a function of its chemical structure and the molecule-substrate interface.

### 4:40pm **EM+NC-WeA10 Phase Selection in TiOPc/Ag (111) Molecular Films: Combined STM:STS Investigations*, *Y.Y Wei***, University of Maryland, College Park, ***S.W. Robey,*** National Institute of Standards and Technology, ***J.E. Reutt-Robey***, University of Maryland, College Park

Titanyl phthalocyanine (TiOPc) has emerged as an important molecular component in building organic electronic devices. Its broad optical absorption spans the near infrared - visible region and high photoconductivity are most promising features, yet a tendency for polymorphism may limit TiOPc applications. Understanding how to control the molecular architecture in thin TiOPc films, and relate structure to electronic properties, is thus an important scientific goal. We present STM/STS studies of growth and two-dimensional crystallization of TiOPc films prepared by vapor deposition on Ag (111). We show how three distinctive TiOPc monolayer phases can be fabricated via flux control. At lowest TiOPc fluxes, a honeycomb phase forms, in which molecules organize into interlocked pairs. This phase optimizes quadrupole attraction and minimizes lateral dipole repulsion between TiOPc neighbors. At medium fluxes, a higher-energy hexagonal phase, stabilized by partly overlapped Pc rings between neighboring molecules emerges. At yet higher fluxes, a triangular network of misfit dislocations, with a characteristic domain size of ca. 14 nm is produced. We present molecular models of these three distinctive phases and describe how the film architecture is controlled primarily by electrostatic TiOPc-TiOPc interactions. Comparative STS Studies of the honeycomb and hexagonal monolayers reveal a metallic-like conductivity for both films. Finally, we show how these different TiOPc phases, employed as substrates for sequential $C_{60}$ deposition, yield distinctive donor-acceptor heterostructures with unique electronic characteristics.

[*] This work has been supported by the Department of Commerce through the Nanomanufacturing Center of NIST, the Nanotechnolgy Fund of NASA, and the National Science Foundation under Surface Analytical Chemistry grant CHE0750203.

5:00pm **EM+NC-WeA11 Spin Polarized Electron Tunneling Through Conjugated Molecules**, ***P. LeClair**, W. Xu, G. Szulczewski, A. Gupta*, University of Alabama

Electron tunneling across organic/inorganic interfaces is important to the performance of organic based electronic devices, such as organic light emitting diodes and organic field effect transistors. However, spin dependent electron tunneling across organic/inorganic interfaces is not well understood.[1] In this presentation we will demonstrate the injection, transport, and detection of a spin-polarized current through pi-conjugated molecules. Specifically we highlight the results for tetraphenyl porphyrin (TPP), but the results are similar for other conjugated organic semiconductors.[2] Tunnel junctions were made by depositing TPP between La$_{0.7}$Sr$_{0.3}$MnO$_3$ (LSMO) and Co electrodes. At cryogenic temperatures the devices show a negative magnetoresistance of 15-25%. A tunneling model that explains the temperature, bias voltage and sign of the magnetoresistance will be presented. In addition, we have directly measured the spin polarization (~37%) for electrons tunneling from Co through TPP monolayers using superconductor Al films as the spin detector. Collectively these results clearly demonstrate that spin polarized electrons tunnel through conjugated organic semiconductors with negligible spin-flipping and suggest that such molecules may find use in spintronic applications. For comparison, we will also present recent results utilizing halogen-substituted benzoic acid self-assembled monolayers as a "model" system. In this case, the presence or abscence of spin-flip scattering during tunneling is highly dependent on the choice of the halogen substituent.

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5:20pm **EM+NC-WeA12 Influence of Structural Ordering on Conductivity of Pentathiophene Based Langmuir-Blodgett Monolayers**, ***Y. Qi**,* University of California, Berkeley and Lawrence Berkeley National Laboratory*, B.L.M. Hendriksen, F. Martin, D.F. Ogletree,* Lawrence Berkeley National Laboratory*, C. Mauldin, J.M.J. Frechet,* University of California, Berkeley*, M. Salmeron*, Lawrence Berkeley National Laboratory

Good understanding of the mechanisms responsible for electrical conduction in organic molecules is essential for the development of organic and molecular electronics. In this study we correlate structural and electrical conduction properties of decyl-pentathiophenyl butyric acid monolayers using a conductance atomic force microscope (C-AFM). We used the Langmuir-Blodgett technique to prepare monolayers on heavily doped p-type Si, mica and flat Au substrates. For all substrates we find that two types of structures coexist in the monolayers: one consisting of compact and crystalline islands; the other phase is poorly packed and contains many holes. The magnitude of the friction on crystalline islands is significantly lower than on the poorly packed structure, while the current is at least an order of magnitude higher on the crystalline islands. Scanning on the well-order phase at high loads destroys the lateral order and reduces the conductivity. Our data show that there is a lateral, structural component to the conduction perpendicularly through the monolayer.

## 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. Manivannan,* 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 CdCl$_2$ treatment, devices showed V$_{oc}$ > 700 mV and J$_{sc}$ > 20 mA/cm$^2$. 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 H$_2$, CH$_4$, and CO$_2$ 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 Å$^3$. Hydrogen and methane absorption near 300 K were 1.0 and 2.2 wt% respectively. Carbon dioxide is absorbed 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 CO$_2$ 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 CO$_2$ per TBC4 molecule. We have used empirical molecular simulation techniques to study the dynamics of CO$_2$ and CH$_4$ 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 CO$_2$, 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 CH$_4$ and CO$_2$ is studied under range of conditions by thermodynamic integration. These data support the experimental observations that these molecules can be reversibly absorbed 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 TiO$_2$ 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 TiO$_2$ electrode. Among the various techniques for the preparation of TiO$_2$ 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 TiO$_2$; 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 $SnO_2$:F coated glass by sol–gel technique; where, an alcoholic solution of tetra-buthylorthotitane 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 $TiO_2$ 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 $TiO_2$ 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 $TiO_2$ 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 $\mu m\ s^{-1}$). 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 $\Delta Y$ 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 $\Delta Y$. 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 $\mu m\ s^{-1}$). 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 V5+ species strongly interact with ceria support promoting a reduction of surface Ce4+ to Ce3+. Upon heating or during reaction surface vanadia reacts with ceria support forming a CeVO4 phase. The active site appears to be V5+–O–Ce3+ 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)

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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. Nurmi,* 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 conduced 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. Goeke, 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 $\lambda_s$ in these materials. Electron spin polarized tunneling is explored with ultrathin layers of the molecular organic semiconductor tris(8-hydroxyquinolinato)aluminum (Alq3) and Rubrene ($C_{42}H_{28}$). 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 ($\lambda_s$) 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, $\lambda_s$ 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/$Al_2O_3$ 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). Recently[1] we have reported successful injection of spin-polarized electrons from an Fe film through an $Al_2$ $O_3$ 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/$Al_2$ $O_3$ 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/$Al_2$ $O_3$/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/ $Al_2$ $O_3$/Si structure. While the zero bias resistance for the Fe/ $Al_2$ $O_3$/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.

[1] B.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 (~$10^7$ A/cm$^2$) 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.

## Nanomanufacturing Focus Topic
## Room: 309 - Session NM+PS+AS-WeA

## Nanomanufacturing I: Plasma Processing and Materials
**Moderator:** R.M. Martin, IBM T.J. Watson Research Center

1:40pm **NM+PS+AS-WeA1 Silicon Nanocrystal Inks: Plasma Processing as a Route to Solution-Processed Silicon Films**, ***U.R. Kortshagen***, *R. Cram, D. Rowe, X.-D. Pi*, University of Minnesota **INVITED**

Colloidal nanocrystals are studied for a wide spectrum of applications from more efficient quantum dot solar cells to printed electronics. While significant advances have been made with chalcogenide semiconductors, similar progress with silicon has been hampered for a long time by the lack of efficient synthesis approaches. However, silicon has the undoubted advantage of being non-toxic, environmentally benign, abundant and cheap. This talk describes a plasma synthesis approach for the efficient synthesis of silicon nanocrystals. Silicon crystals are synthesized in a flow through plasma reactor on time-scales of a few ms. The residence time of the silicon crystals can be used to tailor the nanocrystal size. Dopants can be introduced into the crystals and changes in the photoluminescence properties as well as surface etching studies allow to deduce the dopant location within the nanocrystal. The nanocrystal surfaces can be functionalized with organic ligands that impart solubility to the nanocrystals. By making silicon nanocrystals soluble in organic solvents, inks of doped silicon crystals can be formed that can be used to prepare silicon nanocrystal films through solution processes such as drop coating, spin coating, or ink-jet printing. Laser annealing is used to produce conducting films from the colloidal nanocrystal precursors. Structural and electrical properties of the films are determined with a wide array of characterization techniques. Properties and potential applications of these materials will be discussed.[1]

[1] This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. Partial support is acknowledged by NSF grant DMI-0556163, and by Center for Nanostructure Applications at the University of Minnesota.

2:20pm **NM+PS+AS-WeA3 Vertically Aligned Si Nanostructure Arrays formed using $SF_6/O_2$ Plasma**, ***C. Yang***, *S.H. Ryu, Y.D. Lim, W.J. Yoo*, Sungkyunkwan University, Korea

Arrays of high aspect ratio (>10:1) vertically aligned Si nanostructure were formed in an inductively coupled plasma (ICP) reactor using SF6/O2 plasma without any masks at noncryogenic temperature. Mean diameter of the nanostructure arrays is about 100 nm and the mean height is up to 4.77 um. These nanostructure arrays can be fabricated for large area (>100 cm2). The formation of the nanostructure arrays are studied as a function of time, bias RF-power and O2/SF6 ratio. The processing condition of the SF6/O2 plasma is known to markedly affect the preparation of the nanostructure arrays. O2/SF6 ratio determines the formation of the nanostructure arrays. The nanostructure arrays only could be fabricated when the O2 content is not too low or too high, the range is 0.5< O2/SF6<2.5. Two types of the nanostructure arrays formed because of the different bias RF-power, one is nanohole arrays and another is the nanopillar arrays. The formation of the nanostructure is hole when the bias power is 10 W, but the diameter is only 420 nm after etching 150 s. If the bias power increased to 30 W, the nanopillar arrays appear, the mean height is up to 4.77 um after etching 150s. The etching time is also important for the nanostructure arrays. After etching about 40s, the nanostructure arrays appear abruptly and become longer and longer. But very long time etching has destroyed the nanostructure arrays. The mechanism of the plasma etching for fabricating the nanostructure arrays has been investigated using OES, XPS and SEM analyses. From the analyses, the properties of the plasma and the formed passivation layer are mainly reasons for the fabrication of the nanostructure arrays. The best condition to fabricate a high aspect ratio vertically aligned Si nanostructure arrays is suggested.

2:40pm **NM+PS+AS-WeA4 Structured Growth of Silver Nanoparticles Within a Hydrocarbon Matrix**, ***E. Körner***, *J.F. Lübben, G. Fortunato, D. Hegemann*, EMPA, Switzerland

Low pressure plasma processes enable an extensive variety of surface adjustments for medical applications or technical textiles. Specifically, a modular plasma vacuum chamber provides the base for highly flexible and tailor-made coating technology. Different modification strategies, e.g. activation, etching, plasma polymerization or metallization by sputtering can be used separately or combined with each other. This work presents the combination of plasma polymerization and etching with a co-sputtering process which leads to the formation of a nanoporous polymer matrix with embedded metal nanoparticles. A capacitively coupled radiofrequency power input and an asymmetric reactor geometry allow the production of such multifunctional coatings within in a one-step process. The hydrocarbon matrix is built-up by using ethylene ($C_2H_4$) as a monomer gas. In addition, carbon dioxide ($CO_2$) or ammonia ($NH_3$) is used as the reactive gas, to structure the matrix and add functional groups to the a-C:H network. The deposition rate and the functionality of the coatings are adjusted by the ratio of reactive gas to monomer. With increasing the ratio of reactive gas the functionality of the matrix increases at the expense of the deposition rate. An excess of argon is used in the gas mixture for co-sputtering from a Ag cathode. The growth, distribution and formation of Ag particles are analyzed carefully under different conditions with respect to the gas mixture. The films are investigated with atomic force microscopy and scanning electron microscopy after different growth steps. It can be seen that the particles are more embedded in the matrix for higher film thicknesses and lower reactive gas ratios. Additionally, X-ray photoelectron spectroscopy analyses are performed to evaluate the surface chemistry and Ag surface concentration. For bulk measurements, the overall Ag content is measured with inductively coupled plasma optical emission spectrometry. Target covering or oxidation can decrease the Ag deposition rate and has to be taken into account in determining the optimal plasma conditions. In contrast to magnetron sputtering the Ag particles appear to be bigger with RF sputtering, which could provide a Ag reservoir with a slower release and a better long-term antibacterial effect. This is important for the application of the films as antibacterial coatings, where an optimal antibacterial efficiency for a minimal amount of Ag is desirable.

3:00pm **NM+PS+AS-WeA5 Photoluminescence Brightening from Freestanding Single-Walled Carbon Nanotube Bundles Prepared by Diffusion Plasma CVD**, ***R. Hatakeyama***, *T. Kato*, Tohoku University, Japan

The optical property of single-walled carbon nanotubes (SWNTs) has been the subject of intense interest in recent years, since the discovery of efficient photoluminescence (PL) from isolated semiconducting SWNTs. Because it was believed that the debundle of SWNTs was the inevitable process to capture the PL signal from SWNTs, the bundle forming SWNTs were, in most cases, treated as by-products or impurities causing a spectrum broadening and shifting, and hence their optical features, especially the PL, have not attracted a great deal of attentions so far. Very recently, the PL from bundled SWNTs in an aqueous solution has been reported. Since the PL from bundled SWNTs includes outstanding advantages such as an exemption from a complicated debundle process and easy manipulation, it can be expected that the SWNT-bundle engineering has a great potential for the nanotube-based PL device fabrication. From an industrial point of view, the application of nanotube-PL to the well-organized present semiconductor technology is an inevitable factor, i.e., the establishment of bright PL emission from a solid-state material is considered to be a still remained fundamental problem. In this study we report unique PL features obtained from as-grown vertically-, and individually-freestanding SWNTs prepared by a diffusion-plasma chemical vapor deposition method.[1] The intensity of PL is clearly observed to increase through the morphology transition from isolated to thin-bundled of the freestanding SWNTs.[2] Based on the precise spectrum analysis and equation-based estimation of the PL time trace, the origin of the PL brightening is consistently explained in terms of the exciton energy transfer through the tube bundles. The PL brightening is also revealed to obviously depend on SWNT diameters. Only the small-diameter rich sample can realize the PL brightening, which can be interpreted to be due to the different concentration of metallic SWNTs causing a PL quenching. Since it appears to be possible to fabricate brightly illuminating nanotubes on various kinds of substrates, the bundle engineering with freestanding nanotubes is expected to be a potential candidate for realizing the nanotube-based PL device fabrication.

[1] T. Kato and R. Hatakeyama, Appl. Phys. Lett., 92 (2008) 031502.

[2] T. Kato and R. Hatakeyama, J. Am. Chem. Soc., accepted.

4:00pm **NM+PS+AS-WeA8 Practical Considerations for Implementation of Nanomaterials in Aerospace*, K.D. Humfeld*,** The Boeing Company **INVITED**

4:40pm **NM+PS+AS-WeA10 Large-Scale Production and Metrology of Vertically Aligned Carbon Nanotube Films*, L. Dai,*** *K. Bosnick*, National Research Council Canada

We have successfully produced carbon nanotube (CNT) films (25-50 wafers per load) on a large scale in a commercial Tystar chemical vapor deposition (LPCVD) system. Electron microscopy studies indicate that the CNT films are consisted of densely packed and vertically aligned multi-walled CNTs. A series of catalysts and growth conditions are tested systematically to synthesize high quality CNTs by varying the catalytic metal compounds and the CVD parameters. Both Fe films and ternary metal Cr/Ni/Fe films have been found favorable for the growth of aligned CNT films. To assess the as-grown vertically aligned CNT films, we are developing a general metrology which contains various analytical techniques to qualify the CNT film morphology, size, chirality, homogeneity, purity, dispersion, etc. This metrology uses some of the measurement equipments that are broadly used for material characterizations, including scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, profilometry, contact angle measurement and thermo gravimetric analysis (TGA). The metrology will facilitate quality control and process optimization necessary for industry applications of CNT films.

5:00pm **NM+PS+AS-WeA11 Linewidth Measurements on sub-20 nm HSQ/Graphene Nanostructures*, J.J. Peterson,*** Intel Corporation*, M.A. Rodriguez, V. Tileli,* University at Albany-SUNY*, M. Sprinkle, C. Berger, W.A. de Heer*, Georgia Institute of Technology

Although linewidth measurements of patterned graphene nanoribbons using the high resolution (HR) scanning electron microscope (SEM) have been reported in the literature,[1] it is known that such measurments are generally destructive to the structures which are being measured. Furthermore, due to the destructiveness of the measurement, the critical dimensions may be changing even as the measurement is being made. For this reason, the atomic force microsope (AFM) and scanning probe microscope (SPM)[2] has become an accepted method of linewidth measurement for graphene or hydrogen silsesquioxane (HSQ) on graphene structures, but this methodology is not scaleable to a manufacturing environment. For this reason, it is desired that a more manufacturable method of linewidth measurement may be developed for measurement of critical dimensions of graphene nanostructures. In this talk, we compare linewidth measurements sub-20 nm HSQ/graphene structures using the HR SEM and environmental-SEM (E-SEM) and report that E-SEM measurements will support the necessary resolution to enable linewidth measurements of graphene nanostructures without the damage associated with typical HR scanning electron microscopes. Furthermore, we make a comparison of linewidth measurements using both the SPM and E-SEM and discuss each respective method's advantages and disadvantages.

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

## Nanoscale Devices and Sensors
### **Moderator:** S. Evoy, 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 VG is relative low at around VG =-10 V to -15, 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 VG=-15 V to -20 V. The quantum levels are, however, still remaining. Finally, at relative high gate voltage at VG=-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 hoe at low gate bias, and also shows the coherent oscillation of hole that means the wave nature of hoe 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 0.5um CMOS Technology. Electrical measurements from the assembled SWNTs yield ohmic behavior with a two-terminal resistance of ~44KOhms. 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 100ºC 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 μm, 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 um 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 μm for very narrow metal nanowires well above 4 μm 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 tranversal 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 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, **N. Fitzpatrick***, 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 6M1N1, 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 gluteraldegyde 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/μm2 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/μm2. 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 cantilever[1] 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 controller[2] 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.

[1] Ivo W. Rangelow, Microelectronic Engineering 83 (2006) 1449–1455.

[2] PLLpro, 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 $Cl_2$ 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 $Cl_2$ 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 $Cl_2$ 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 turn on, a much larger pressure rise was observed due to delayed (i.e., Langmuir-Hinshelwood) recombination of Cl atoms. Recombination coefficients, $\gamma_{Cl}$, ranged from 0.004 to 0.03 and increased with Cl-to-$Cl_2$ number density ratio before reaching some plateau for Cl/$Cl_2$ > 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, $Cl_2$, $Cl^+$, $Cl_2^+$, 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/$Cl_2$ number density ratio, model predictions of Cl and $Cl_2$ densities in surface-wave and inductively coupled plasma reactors with both stainless steel and anodized aluminum walls will be compared with measured Cl and $Cl_2$ 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,* Universite 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 $O_2$-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 $O_2$ 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 $O_2$. 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 $\gamma_O = 0.10$ 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 ~$10^{11}$ cm$^{-2}$, depositing a small fraction of a monolayer (~5 x $10^{14}$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 $\gamma_O$ The surface was further exposed to the Cu doses of ~2, 3, and 8 x $10^{11}$ cm$^{-2}$. Each added dose causes $\gamma_O$ to increase accordingly. At 8 x $10^{11}$cm$^{-2}$ $\gamma_O = 0.15$. Much larger doses (~3 x $10^{13}$ cm$^{-2}$) resulted in detectable Cu on the surface and a $\gamma_O$ of ~0.3.

2:20pm **PS1-WeA3 Impact on Wafer to Wafer Repetability of Cleanning/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 $Al_2O_3$ and $Y_2O_3$ Surfaces by Irradiations of High Density $CF_4/O_2$ and $SF_6/O_2$ 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 (AlOxFy and/or AlFx) 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 CFx (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 SFx (x=1-5) radicals and Al-O would be lower than that of CFx, 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 (YOxFy and/or YFx) 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.

[1] G. Cunge, et. al., Plasma Sources Sci. Technol. 14, 599 (2005)

[2] K. Miwa and T. Mukai, J. Vac. Sci. Technol. B 20, 2120 (2002)

[3] K. Miwa, et, al., Proceedings of the IEEE. ISSM 2007, PO-O-210, 479 (2007)

[4] M. Aramaki, et. al., Jpn. J. Appl. Phys. 43, No.3, 1164 (2004)

[5] J. 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 DF+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 +/- 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/$O_2$ resist trimming processes will induce a 50% decrease in LWR (initial LWR ranging from 18 to11 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 smoothening. 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. Jinnnai, 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. Himpsel, 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 $SF_6$ 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.

## Plasma Science and Technology
## Room: 306 - Session PS2-WeA

## Plasma Diagnostics, Sensors, and Control I
## **Moderator:** J.P. Booth, Lam Research Corporation

1:40pm **PS2-WeA1 Novel On-Wafer RF-Current Sensor: Sheath Impedance and Plasma Density**, ***M.J. Titus***, *D.B. Graves*, University of California, Berkeley

"On-wafer" plasma sensors are new metrology tools that provide spatially-resolved wafer-state and/or plasma information. Measuring the temporal and spatial evolution of wafer-surface and adjacent plasma characteristics is the key to developing advanced plasma tool control schemes. One such commercially available sensor is the PlasmaVolt$^{TM}$ device, developed by KLA-Tencor. We utilize a 150 mm diameter version of the commercial product consisting of an on-board electronics module with wireless communication that allows data storage of 2 RF-current sensors embedded on the wafer at different radial positions. We report results using this device in an inductively coupled plasma with RF-biased substrate under a range of conditions. Electron density and temperature are independently measured above the wafer using a Langmuir probe and the positive ion current to chamber walls is measured with a shielded planar probe. The RF-voltage and current waveforms applied to the substrate are measured with a digital oscilloscope. The quantitative relation between the PlasmaVolt$^{TM}$ sensor wafer measurement and the adjacent electron density is established using a fluid sheath model. We demonstrate with this combined experimental-modeling approach that the plasma density scales with the RF-current sensor measurements but the nature of the scaling is dependent on the sheath impedance. When the sheath impedance is predominately capacitive (corresponding to relatively low electron density and high RF-bias voltage) sensor measurements are proportional to the square-root of the electron density. When sheath impedance is more resistive (corresponding to relatively high electron density and low RF-bias voltage), the sensor measurement is proportional to electron density.

2:00pm **PS2-WeA2 In-situ Diagnostic to Measure Charging During Plasma Etching**, ***E. Ritz***, *M.J. Neumann, J.A. Hoban, D.N. Ruzic*, University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, it is known that defects can occur such as trenching, bowing, and twisting. These defects are particularly noteworthy in the manufacture of DRAM deep-trench capacitors. In order to investigate the role of charging on these phenomena an in-situ diagnostic was fabricated using photolithographic and deposition techniques. The device consists of alternating layers of conducting and insulating materials. During the construction of the device, vias are integrated into the layout, extending all the way from the top surface to the substrate. The insulating layers create discrete measurement layers, provided by the conducting layers (electrodes). The electrodes are attached to voltage measurement leads and can then be used to measure the build up of sidewall charging at different heights along the via when exposed to a plasma. To determine the effect of geometry, if any, on charging, several aspect ratios were used by maintaining the same device thickness but varying the diameter of the vias. The entire stack is less than one micron thick, with vias ranging in diameter from 1 micron to 100 nanometers, thereby producing aspect ratios of 1:1 to 10:1. In addition, a macroscopic parallel to the diagnostic was constructed in order to compare how overall size of the features affects the charging properties. The macroscopic device is on the order of 1cm thick with features on the order of 1mm in diameter. The transition from macroscopic to microscopic gives a better understanding of the transport and charging phenomena involved in constructing DRAM features and at what scale they are significant. Conducting layers for the macroscopic device are metal and the insulating layers are ceramic. Plasma and charging experiments were conducted in a commercial silicon dioxide etch chamber. Typical ion fluxes measured on the order of $10^{17}$ ions/cm$^2$*sec. At 500W of 2.0 and 2.2 MHz power on each of the coils (1000W total), a plasma density of $2*10^{12}$ +/- $5*10^{11}$ cm$^{-3}$ and electron temperature of 3 +/- 0.3eV was measured at 0.3+/-0.2 mm about the substrate at 4.5+/-1 cm from the edge of a 20cm chuck. RF variations in the signal were observed at the two driving frequencies and at the beating frequency of 150kHz, as expected. Results from the diagnostics will be shown for various plasma conditions and compositions.

2:20pm **PS2-WeA3 Time Dependence of Charge-Build-up Voltages in Production Etcher by On-Wafer Real Time Monitoring System**, ***J. Hashimoto***, *T. Tatsumi, S. Kawada, N. Kuriyama*, Miyagi Oki Electric Co., Ltd., Japan, *I. Kurachi*, Oki Electric Industry Co., Ltd., Japan, *S. Samukawa*, Tohoku University, Japan

Charge-build-up during plasma etching process is one of crucial issues to realize nano-scale devices. Because gate insulator thickness of such devices is shrunk down to 1nm range, the gate insulator breakdown caused by the charge-build-up is a key issue and has to be solved. To understand the phenomenon of the charge-build-up, it is absolutely necessary to monitor the time dependence of charge-build-up precisely. We have advanced charge-build-up monitoring sensors proposed by Dr.Samukawa. We have monitored etching parameters dependency and aspect ratio dependency in steady status in production etcher and have demonstrated effectiveness of the sensors. However, it was difficult to monitor charge-build-up phenomenon in unsteady status in detail. Therefore, we developed On-Wafer Real Time Monitoring System which can measure the data of charge-build-up voltages at the timing of several micron seconds and can record charge-build-up voltages in processing in production etcher. In general, the recipes in production etchers have several sequential etching steps. Unstable plasma tends to occur especially at the time of chucking wafer electro-statically, turning on-off plasma discharge and switching the etching step. As a result, they induce plasma damages. Therefore, it is important to monitor charge-build-up voltages not only in steady status, but also in unsteady status. In this study, we monitor the time dependence of charge-build-up voltages in processing in production etcher by On-Wafer Real Time Monitoring System and the charge-build-up phenomena in unsteady status will be discussed in detail in the presentation.

2:40pm **PS2-WeA4 Origin of Electrical Endpoint Signals in Rf-biased, Inductively Coupled Plasma Etching**, ***M.A. Sobolewski***, *D.L. Lahr*, National Institute of Standards and Technology

When a plasma etch consumes one layer and exposes an underlying layer, changes are detected in measured electrical parameters, such as the dc self-bias voltage and the voltage, current, impedance, and phase at the fundamental and harmonic frequencies. Consequently, these electrical signals are widely used for endpoint detection, i.e., for determining when to terminate an etch. However, the mechanisms responsible for the observed electrical changes are not well understood. The electrical changes may indicate a change in plasma electron density and ion flux caused by changes in the gas-phase densities of etch products and reactants that occur as an etch proceeds to completion. Alternatively, changes in substrate electrical properties or surface properties such as work function and the yield of secondary and photoemitted electrons may be involved. To investigate these mechanisms, experiments were performed in an inductively coupled plasma reactor equipped with rf bias and a wave cutoff probe. The cutoff probe[1,2] allowed small changes in the plasma electron density to be measured with good accuracy and resolution, on a time scale of a few seconds, regardless of the presence or absence of insulating layers on probe surfaces. Simultaneous measurements of electrical signals and cutoff probe data were made during CF$_4$/Ar plasma etches of thermal silicon dioxide films on silicon substrates. Changes observed in the components of voltage, current, impedance and phase at the rf bias frequency were related to, and fully explained by, changes in plasma electron density measured by the cutoff probe. The dc self-bias voltage and harmonic signals showed more complicated behavior that cannot be explained solely by changes in plasma electron density. The results allow several general conclusions to be drawn about the relative reliability and usefulness of endpoints obtained from each of the different electrical signals.

[1] M. A. Sobolewski and J.-H. Kim, J. Appl. Phys. 102, 113302 (2007).

[2] J.-H. Kim, S.-C. Choi, Y.-H. Shin and K.-H. Chung, Rev. Sci. Instrum. 75, 2706 (2004).

3:00pm **PS2-WeA5 Local and Non-Local Changes of Plasma Parameters in an Expanding Thermal Plasma Reactor Coupled with a Pulse-Shape Substrate Biasing Technique**, ***P. Kudlacek***, *R.F. Rumphorst, M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

The control of the flux and energy of ions bombarding the substrate is crucial to enhance deposited film properties or etch rate at, for example, low substrate temperatures or in weak remote plasmas. The most widespread method for these purposes is biasing because of its simplicity and suitability for operation with both conductive (dc bias) and dielectric (rf or pulsed bias) substrate. Recently, pulsed bias became subject of increased interest mainly due to lower and controllable heat load of the sample and, considering that rf bias inherently leads to bimodal energy distribution of ions bombarding the biased substrate (IED), also a promising technique to reach narrow almost unimodal IED. When pulse-shaped bias voltage is connected to the substrate holder the sheath rebuilding at the beginning of on-pulse and the ion-induced secondary electron emission during the pulse can lead to production of significant amount of fast electrons which can non-locally affect the plasma and near-wall sheath potential as has been reported by Demidov at al. (2005 Phys. Rev. Lett. 95 215002). Therefore, an effect of local and non-local changes of plasma parameters in a reactor with substrate holder biased by pulse-shaped voltage was studied in this work. Non-local changes are discussed on the basis of the electron temperature $T_e$ and ion density $n_i$ which are determined spatially using a double Langmuir probe technique, while the distribution function of ions bombarding the biased substrate shows local effects of biasing such as additional generation of ions driven by bias voltage and influence of collisions. IEDs are measured by means of a retarding field energy analyzer. Two limit biasing conditions are presented for comparison, namely dc bias and 13.56 MHz rf bias which shows practically no and strong (e.g. almost 5 times higher $T_e$ in the distance of 30cm from the biased substrate holder) non-local plasma parameters affection, respectively. All experiments were run in a remote expanding thermal plasma (ETP) reactor, in Ar and $Ar/N_2$ gas mixture compositions under several pressures (up to 35 Pa). The substrate holder was negatively biased (up to -300V) by means of a home designed pulsed power supply operating with a frequency of up to 200 kHz and a variable duty cycle.

### 4:00pm **PS2-WeA8 Plasma Diagnostics by a Coaxial Resonant Cavity**, ***S. Kobayashi***, Applied Materials Inc.

Microwave plasma diagnostics were developed mainly in the field of microwave and plasma interaction. Recently, these methods have also been adopted for plasma dischargers. The main advantages of microwave diagnostics are; (a) the capability to measure directly a plasma electron density and, (b) the applicability in a process gas environment. Intended to use in dischargers, new devices (e.g. plasma absorption probe, U-shape probe, plasma microwave interferometer) were developed based on the microwave method in the last decade. However, when these open structural probes are used in a small chamber, radiation from the probe surface cannot be neglected, resulting in random resonances caused by interference with a chamber wall. To resolve this issue, a coaxial resonant cavity is developed, which is open for plasma diffusion, while it is closed with respect to microwave radiation. In vacuum, the cavity is designed to have a sharp resonance in a 2-4 GHz band. When plasma is generated in a chamber, the resonant frequency up-shifts due to a change in the effective dielectric constant. Once the resonant frequency is given as a function of a loaded electron density, the electron density is measured by monitoring a frequency-shift. Preliminary measurements of electron plasma density of Argon and Nitrogen showed good agreements with those of a Langmuir probe. Theoretically, this probe can measure the electron temperature of a plasma, since the electron temperature can be represented as a function of variation in the quality factor of a resonance in the cavity. This possibility will be also studied and discussed in the paper.

### 4:20pm **PS2-WeA9 On Detection and Prevention of Plasma Instabilities**, *V.L. Brouk, **D.C. Carter**, R.L. Heckman*, Advanced Energy Industries, Inc.

The presence of instabilities in low pressure (5 to 100 mT) electronegative plasmas is well documented. In inductively driven plasmas instabilities often exist between the stable low density, capacitive mode and the stable high density, inductive regions causing oscillations in particle density, optical emission and coil voltage. Instabilities also occur in capacitively coupled plasmas driven similarly by electron attachment to electronegative species. Oscillation frequency can range from less than a 100 Hz to greater than 10 kHz and can depend on multiple process parameters including pressure, gas flow, gas mixture and power level.[1,2] Especially for high efficiency, switch mode power amplifiers, interaction between the power-dependent plasma impedance and the load-dependent amplifier response can promote or aggravate unstable behavior. This interaction involves complex impedance trajectories having both magnitude and angle components when displayed in the impedance plane. The common practice of adjusting transmission cable length shifts the phase angle of the amplifier portion of the interaction and thus minimizes the combined feedback to achieve a stable operating state. For a singular set of conditions, the point of transition from one mode to the next can be well defined and effectively addressed in this manner. But complete mapping of such behaviors across a broad process space is not practical due to the enormous number of variables present in modern plasma processes. Further, adjustments of physical cable length can be problematic in many applications. For these reasons a convenient means for predicting the onset of plasma instabilities and ideally a method for avoiding an unwanted transition to unstable operation is desirable. In this study we demonstrate a quantitative diagnostic for assessment of plasma stability providing a measure of margin from an unstable threshold. When used with a properly equipped RF amplifier, the technique provides context necessary to avoid the onset of instability in these plasmas. Using a fixed transmission cable and minor adjustments in RF frequency to adjust the electrical wavelength, we show how this method can be used to actively stabilize both low and high frequency plasma oscillations.

[1] A. M. Marakhtanov, et. al., J. Vac. Sci. Technol. A 21 (6), Nov/Dec 2003, 1849-1864.

[2] A. Descoeudres, et. al., Plasma Sources Sci. Technol. 12 (2003), 152–157.

### 5:00pm **PS2-WeA11 Secondary RF Plasma Assisted Closed-Field Dual Magnetron Sputtering System for ITO Thin Film Deposition on Plastic Surfaces**, ***L. Meng****, *R. Raju*, University of Illinois at Urbana-Champaign, *T. Dockstader*, Kurt J Lesker Company, *H. Shin, D.N. Ruzic*, University of Illinois at Urbana-Champaign

Since the demand keeps growing for larger size plasma displays, and for inexpensive flexible displays on plastic or other organic substrates, it is important to develop a plasma processing device to handle large size substrates, while maintain the uniformity and quality of deposited materials without damaging the substrate. An RF plasma-assisted closed-field dual magnetron sputtering system investigated in this study is the prototype of such a system. The prototype consists of two 3 inch DC magnetrons which can be operated at both balanced and un-balanced (closed-field) configurations. This system enhances the plasma density, metal ionization fraction and has the ability to produce high quality films at lower substrate temperature. An RF coil was fabricated, installed in between the magnetrons to initiate secondary plasma. A RF compensated Langmuir probe was used to diagnose the spatial distribution of argon sputtering plasma. In the constant current mode (50 mA) of the magnetrons, the RF plasma enhances the electron density to one-order of magnitude higher compared with no RF plasma and results in an increase in the deposition rate. The ionization fraction of the sputtered materials was measured using the QCM combined with electrostatic filters. The presence of RF plasma effectively enhanced the ionization fraction of the sputtered metal flux to about 90%. The performance of the closed-field magnetron configuration was compared with the balanced one. Enhancement in the electron density is observed in the closed-field magnetron configuration near the substrate which is twice as large compared to the balanced one. Experiments were conducted on the deposition of ITO on glass and plastic substrates at closed-field configuration. Wide range of operating parameters has been investigated to get highly transparent and conducting films. ITO thin film with 91% of transparency and resistivity of 30 Ω/square was obtained at the magnetron current of 90 mA, pressure of 5 mTorr, 2.5% of $O_2$ fraction in Ar, the RF power of 225 W, and substrate temperature was well kept below 120 °C. Results on the optimization of the operating parameters for high quality ITO film will be presented. Surface morphological studies have been carried out on the film using both balanced and un-balanced configurations. Results from extending this system to larger rectangular shaped magnetrons in a real flat panel display manufacturing system will also be presented.

### 5:20pm **PS2-WeA12 Optical and Electrical Diagnostics of an Arc Plasma Jet under Atmospheric Pressure**, ***C.Y. Wu***, National Taiwan University, *C.W. Chen, W.C. Cheng*, Industrial Technology Research Institute, Taiwan, *C.C. Hsu*, National Taiwan University

An arc plasma jet under atmospheric pressure was studied. This plasma jet is able to generate stable plasma sustained by a DC pulsed power of 20 kHz ~ 40 kHz using nitrogen and clean dry air. A voltage probe and a current probe were used to characterize the voltage and current waveform of this plasma jet. The optical emission at this plasma jet downstream was monitored by an optical emission spectrometer. Multiple thermocouples were used to measure the downstream jet temperature. The current and voltage waveforms showed glow-to-arc-transition-like characteristics. It is found that the time-averaged current increases with the power input and is not sensitive to the flow rate. The peak current, however, increases as the applied power decreases and as the flow rate increases. The peak current remains below 1.0 A under high power and low flow rate conditions while reaches 3.0 A for low power and high flow operation regimes. It suggests that the peak current is not directly controlled by the amount of power input to the plasma. Optical diagnostics shows nitrogen molecular emissions dominate in nitrogen plasma jets. The nitrogen plasma jet temperature appears to be higher than the temperature of the air plasma jet as measured by the thermocouples at the jet downstream. The detailed discharge mechanism will be presented and its implications in materials processing will be discussed.

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* PSTD Coburn-Winters Student Award Finalist

## 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 $TiO_2$ with a high refractive index. Stoichiometric $TiO_2$ 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 $TiO_2$ 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 $TiB_2$ 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 intio 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 MoNx 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 (VxO3X-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 in[3] 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. Högberg, 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, VV. 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, ICMCTF, 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. Gorokhovsky****, C. Bowman, D. VanVorous, J. Wallace*, Arcomac 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 oxi-ceramic 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 oxi-ceramic 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.

## Surface Science
## Room: 208 - Session SS1-WeA

## Structure of Oxide Surfaces and Oxide Heterostructures
## **Moderator:** Ch. Wöll, Ruhr-University, Germany

1:40pm **SS1-WeA1 Tuning the Properties of Metals on Oxides: Au on MgO a Case Study**, ***T. Risse***, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany **INVITED**

This contribution will focus on the recent efforts to characterize the properties of Au atoms and particles on well ordered MgO films and the ability to tune these properties by modifying the oxide film. The studies are embedded in the current endeavor to correlate the properties of oxide supported Au deposits with their catalytic activity. In this respect the charge state of Au particles has come under scrutiny, in particular after combined theoretical and experimental evidences suggested that nucleation of Au clusters at point defects of MgO leads to a charging of the particles which in turn was made responsible for the enhanced catalytic activity in low-temperature CO oxidation. More recently theoretical calculations predicted that not only defects sites might be able to induce charging of Au atoms and cluster, but the film thickness may serve a suitable parameter to control charging.[1,2] In this contribution we present a combined low-temperature scanning tunneling microscopy/spectroscopy (STM/STS), infrared (IR), and electron paramagnetic resonance (EPR) spectroscopic investigation on the properties of gold atoms and clusters adsorbed on well ordered MgO films. These studies aim at providing experimental evidences for the presence of negatively charged Au atoms and particles on these oxide surfaces. First we will focus on the impact of color centers. To this end STM/STS and EPR spectroscopic results will be discussed which can be used to characterize these centers and prove the adsorption of Au particles on them. In combination with IR spectroscopy it possible to show that color centers are indeed capable to donate charge onto Au particles. As a second part we want to discuss the question if the MgO film thickness is a suitable parameter to tune the charge state of Au deposits as predicted theoretically. Thereto low temperature STM experiments of Au atoms and clusters deposited on 3 ML and 8 ML thick MgO films will be discussed to find evidences for a charge transfer for 2-3 ML thick MgO films.

[1] G. Pacchioni, L. Giordano, M. Baistrocchi, Phys. Rev. Lett. 94, 226104 (2005).

[2] D. Ricci, A. Bongiorno, G. Pacchioni, and U. Landman, Phys. Rev. Lett. 97,036106 (2006).

2:20pm **SS1-WeA3 Shape Transitions of Anatase Islands during Epitaxial Strained Layer Growth**, ***M.S.J. Marshall****, M.R. Castell*, University of Oxford, UK

It is well established that misfit strain between epitaxial islands and their substrates significantly influences the shape evolution of the islands as they increase their volume during growth. We have studied the growth of anatase islands on $SrTiO_3$ surfaces. Extended annealing in UHV causes the surface region of single crystalline $SrTiO_3$(001) to become enriched with $TiO_2$. This results in the formation of epitaxial islands of anatase $TiO_2$ (001). These islands are studied using UHV scanning tunneling microscopy (STM) and UHV scanning electron microscopy (SEM), which reveals the changes in morphology during growth induced by misfit strain. Screw dislocations observed with STM on some of the islands enable the rapid growth of micron-sized square islands. Starting from a square island, two types of shape transitions are observed. In the first, above 1000°C, the square anatase islands elongate in length and narrow in width. This growth behavior follows the established Tersoff and Tromp model of strain relief in epitaxial islands.[1] In the second growth mode, below 1000°C, the islands relieve strain by the formation of trenches in the middle of each side of the square, thereby evolving into crosses. This shape arises because a lower annealing temperature imposes a kinetic constraint on the detachment of growth units necessary for island narrowing. While it might be expected that the growth of the notches would proceed to form four squares, each of optimal dimension, this does not occur. The shape transitions occur because the strain energy term in square islands increases more rapidly with volume than the surface and interface energy terms. In our system the islands are widely spaced, thus avoiding inter-island interactions, but there are still substantial differences between the theoretically predicted critical island size of a few 10s of nm edge length and our observed 1μm length. This can probably be explained because of partial strain relief due to dislocations in the anatase islands.

[1] J. Tersoff, and R. M. Tromp, Phys. Rev. Lett. 70, 2782 (1993).

2:40pm **SS1-WeA4 SEM Controlled STM Characterization of Cu/ZnO Nanoparticles**, ***A. Birkner***, *V. Schott, Z. Wang, Ch. Wöll*, Ruhr-Universität Bochum, Germany

The investigation of Cu deposits on ZnO substrates is of significant importance for understanding methanol synthesis using $Cu/ZnO/Al_2O_3$ catalysts. The role of the Cu is still under debate. Whereas some authors propose that the active sites are on the surface of bare Cu particles, others suggest that under reaction condition the surface in fact is covered by a thin layer of ZnO. In order to resolve this issue we have investigated temperature induced morphology changes of Cu islands deposited on ZnO substrates. We have extended the STM investigations of Kroll and Köhler[1] by additionally employing scanning electron microscopy (SEM). Our combined SEM/STM instrument allows to investigate Cu nanoparticles directly after deposition and heating and after exposure to reactants at pressures up to 1 bar. With the help of the SEM the very same Cu particle can be addressed before and after gas-phase exposure. By additionally employing Auger spectroscopy we can determine the composition of the surfaces of the Cu particles. We will also present first STM measurements of Cu clusters deposited on ZnO powder particles.

[1] M. Kroll, U. Köhler, Surf. Sci. 601 (2007) 2182.

3:00pm **SS1-WeA5 Preparation of $TiO_2$ Nanocrystals by Oxidation of Ti-Au Surface Alloys**, ***D.V. Potapenko***, *R.M. Osgood*, Columbia University

The formation of $TiO_2$ nanoparticles on a non-reactive, single-crystal noble metal substrate is useful for studies of nanocatalytic reactions. The formation of Ti-Au surface alloy on Au(111) surface and the growth of $TiO_2$ nanocrystals from the surface alloy have been studied with scanning tunneling microscopy (STM), scanning tunneling spectroscopy (STS) and Auger electron spectroscopy (AES). In our study, titanium was vapor deposited on Au(111) surface at 200 K. STM images show that Ti nucleates at the elbows of the surface herringbone reconstruction. At low Ti coverages (< 0.3 ML) extensive surface alloying occurs already at 400 K through island – substrate atomic exchange. Yet even at 900 K some amount of Ti stays near the surface. The exposure of the sample at 900 K to the flux of $O_2$ leads to oxidation of this sub-surface Ti and to growth of $TiO_2$ nanocrystals. At low initial Ti coverages (< 0.1 ML) the majority of the crystallites have triangular shape and at higher coverage, we observe hexagonal and ridge-like crystallite formation. The results of our experiments form an interesting comparison to recent studies of $TiO_2$ nanocrystals formed via reaction of vapor-deposited Ti on water multilayers on Au(111).

4:00pm **SS1-WeA8 Interface and Electronic Characterization of Thin Epitaxial $Co_3O_4$ Films**, ***C.A.F. Vaz***, *H.-Q. Wang, C.H. Ahn, V.E. Henrich, M.Z. Baykara, T.C. Schwendemann, N. Pilet, B.J. Albers, U.D. Schwarz*, Yale University, *L.H. Zhang, Y. Zhu*, Brookhaven National Laboratory, *J. Wang, E.I. Altman*, Yale University

The oxides of the 3d transition metals form an important class of materials with properties that depend sensitively on the cationic oxidation state and the electronic environment. As a consequence, these compounds display a multiplicity of magnetic, electronic and catalytic behavior, which makes them interesting from both fundamental and practical perspectives. In this work, we study the interface and electronic structure of thin (~20-74 nm) $Co_3O_4$(110) epitaxial films grown by oxygen-assisted molecular beam epitaxy on $MgAl_2O_4$(110) single crystal substrates. Using several real and reciprocal space techniques, we show that the surface and bulk properties of [110]-oriented $Co_3O_4$ thin films depend sensitively on growth conditions and post-growth annealing. The as-grown film surfaces are found to be relatively disordered and exhibit an oblique low energy electron diffraction (LEED) pattern associated with the O-rich $CoO_2$ bulk termination of the (110) surface. Post-annealing is found to improve considerably the film characteristics; in particular, the film surface displays sharp rectangular LEED patterns, suggesting a surface stoichiometry of the alternative $Co_4O_4$ bulk termination of the (110) surface. Non-contact atomic force microscopy demonstrates the presence of wide terraces separated by atomic steps in the annealed films that are not present in the as-grown structures; the step height of ~2.7 Å corresponds to two atomic layers and confirms a single termination for the annealed films, consistent with the LEED results. Finally, magnetic susceptibility measurements show that antiferromagnetic order is present at low temperatures, with an ordering temperature close to 47 K for the as-grown films and of about 30 K for the annealed films. Such well characterized and high quality surfaces could be employed as templates for the growth of other materials or as a model system for the study of exchange bias.

4:20pm **SS1-WeA9 Surface Structure of ZnO(0001) Nanolayers on Pd(111)***, *G. Weirum*, Karl-Franzens University Graz, Austria, *R. Schennach, A. Winkler*, Graz University of Technology, Austria, *I. Bako*, Chemical Research Centre of the Hungarian Academy of Science, Hungary, ***S. Surnev***, *F.P. Netzer*, Karl-Franzens University Graz, Austria

Zinc oxide has attracted a significant scientific and technological interest since it is widely used in catalysis, gas sensing, and in the fabrication of optoelectronic devices. When the wurtzite ZnO crystal is cleaved parallel to the basal plane (0001), two structurally and chemically different surfaces are created on each side of the crystal, which are Zn- and O-terminated. The structure stabilisation mechanism of these two polar surfaces has been extensively investigated,[1,2,3,4] but consensus models have not evolved yet. When prepared in a nanolayer form (1-2 monolayers thick), ZnO has been shown to adopt a hexagonal boron–nitride structure, where the Zn and O atoms are arranged in a trigonal planar (i.e. non-polar) configuration.[5] Here we have studied the surface structure by scanning tunnelling microscopy (STM) and low energy electron diffraction (LEED) of ZnO nanolayers grown on a Pd(111) surface as a function of the Zn coverage and the oxygen pressure. ZnO layers have been prepared either by reactive evaporation of Zn in oxygen atmosphere ($5x10^{-8}$–$5x10^{-6}$ mbar) onto the Pd substrate or by post-oxidation of Zn metal deposits, both methods yielding similar results. In the submonolayer coverage range two two-dimensional hexagonal ZnOx phases coexist on the Pd(111) surface: one of them exhibits an open honeycomb structure with a surface periodicity of ~ 11 Å, whereas the other one has a close-packed structure with a lattice constant of 3.3 Å, which is close to the bulk value of ZnO(0001) surfaces (3.25 Å). The latter phase becomes dominant at higher oxygen pressures and also at higher Zn coverages. The first ZnO monolayer on Pd(111) contains the hexagonal close-packed layer phase only and displays a (6x6) Moiré structure. At higher coverages the flat film morphology is maintained, but two different terminations are resolved in STM, which are found to show pronounced oxygen pressure dependence.

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[5] C. Tusche et al., Phys. Rev. Lett. 99, 026102 (2007)

*Supported by the Austrian Science Funds (FWF) via the Project P19198-N02 and the National Research Network "Nanoscience on Surfaces".

4:40pm **SS1-WeA10 Growth of Au on Single Crystalline Anatase $TiO_2$(101) and (001): Probing Under-Coordinated Sites with Core Level Photoelectron Spectroscopy**, ***L.E. Walle***, Norwegian University of Science and Technology, Norway, *S. Plogmaker*, Uppsala University, Sweden, *A. Borg*, Norwegian University of Science and Technology, Norway, *A. Sandell*, Uppsala University, Sweden

Gold has for a long time been regarded as an inert surface of little use as catalyst. However, in the last decade gold particles have begun to garner attention for their unique catalytic properties.[1] Supported gold particles on metal oxides have been shown to be effective catalysts for several processes, including CO oxidation at remarkably low temperatures, down to 200 K. Most intriguing is the strong size dependence, particles below 5 nm in size are far superior to larger particles in terms of catalytic activity.[2] The detailed mechanism behind the CO oxidation process on the Au/$TiO_2$ system is still largely an enigma. Many studies have suggested under-coordinated Au atoms and the Au-$TiO_2$ interface as reactive sites. A fundamental understanding of the growth mechanism of Au clusters on $TiO_2$ and the nature of the Au/$TiO_2$ bond is thus of great importance. Up till now most experimental studies of Au particles on single crystal $TiO_2$ have been done on the rutile phase, due to the good availability of rutile single crystals. On the other hand, the anatase $TiO_2$ polymorph seems to be the preferred phase when forming nanosized particles. In the last couple of years good quality anatase single crystals have become commercially available which has triggered an increased research interest. In this contribution we present a study of Au growth on single crystalline anatase $TiO_2$(101) and $TiO_2$(001) surfaces under UHV conditions using core level photoelectron spectroscopy. The data were obtained at the Swedish National Synchrotron Facility MAX II. A preliminary analysis gives that Au nucleates at steps on both surfaces. Regarding the (101) surface this is in agreement with a recent report by Gong et al.[3] In addition, we have studied subsequent adsorption of CO at 120 K on the Au particles. Adsorption of CO induces a shift of the Au 4f core level by 1 eV, which is easily observed. The relative amount of Au atoms that can bond to CO varies with the amount of deposited Au. Since CO only bonds to under-coordinated Au atoms at 120 K the results thus give information regarding the geometrical properties of the Au particles.

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5:00pm **SS1-WeA11 Growth of CeOx Nanoparticles on $TiO_2$(110)**, ***J.B. Park***, *D.J. Stacchiola, J. Graciani, S. Ma, A. Nambu,* Brookhaven National Laboratory, *J.F. Sanz,* Universidad de Sevilla, Spain, *J.A. Rodriguez, J. Hrbek*, Brookhaven National Laboratory

Catalysts containing nanoparticles of ceria supported on titania exhibit a high activity for the water-gas shift reaction and the CO oxidation. It has been suggested that this catalytic activity is related to the easy reversible change of the oxidation states of ceria ($Ce^{3+}$ and $Ce^{4+}$), but very little is known about the ceria-titania interactions and the growth mode of ceria on titania. In this work, the growth of CeOx on rutile $TiO_2$ (110) have been investigated by STM and PES in UHV. The deposition of CeOx changes the morphology of $TiO_2$ (110), creating several layers deep steps. At low coverages (less than 0.3ML of Ce), CeOx nanoclusters are preferentially nucleated on the in-plane oxygen atoms of $TiO_2$ (110) and exhibit diagonal arrays along the [001] direction by sharing bridging oxygens. At high coverages, extended rectangular islands of CeOx are observed. XPS studies show that the diagonal arrays of CeOx nanoclusters and their coverage-dependent morphological changes are associated with changes in the oxidation states of the CeOx nanoparticles. The DFT calculations provide the detailed atomic structures for CeOx on rutile $TiO_2$ (110).

This research was carried out at Brookhaven National Laboratory and supported by the US Department of Energy (Chemical Sciences Division, DE-AC02-98CH10886).

5:20pm **SS1-WeA12 Experimental Band Dispersions and Surface Morphology of the Wide Band Gap Oxide Semiconductor β-$Ga_2O_3$ With and Without Mn Doping**, ***T.C. Lovejoy***, *J. Morales, E.N. Yitamben,* University of Washington, *N. Shamir,* Nuclear Research Center - Negev, Israel, *S. Zheng, S.C. Fain, F.S. Ohuchi, M.A. Olmstead*, University of Washington

Experimental studies of the wide band gap semiconductor β-$Ga_2O_3$ have been conducted on bulk single crystals using angle resolved photoemission (ARPES) and scanning tunneling microscopy (STM). This system exhibits interesting electronic and optical properties including electroluminescence and resistivity changes upon gas adsorption. In addition, the resistance can vary over many orders of magnitude with annealing and/or electric field treatment of the transparent crystal. Measured valence band dispersion relations are in qualitative agreement with previously reported theoretical calculations. The observed local surface structure is similar to that previously reported for thin films, but the larger scale morphology is characterized by rectangular pits or islands a single unit cell high with lateral sizes varying on the 10-100nm scale. Preliminary experiments with transition metal (Mn) doping reveal changes in electronic structure and surface morphology that may be relevant for application of Mn:$Ga_2O_3$ as a dilute magnetic oxide. Work supported by NSF grant DMR-0605601. TCL was supported by an IGERT Fellowship, NSF/NCI DGE 0504573; ENY was supported by an IBM Fellowship. Some experiments were performed at the Advanced Light Source, Berkeley, supported by DOE contract DE-AC02-05CH11231.

## Surface Science
## Room: 209 - Session SS2-WeA

## Electrons and Electronic Spectra at Surfaces
## **Moderator:** R.M. Osgood, Columbia University

1:40pm **SS2-WeA1 Electron Dynamics at a Metal-Organic Interface**, ***C.H. Schwalb***, *M. Marks,* Philipps University Marburg, Germany, *S. Sachs, A. Schöll, F. Reinert,* University Würzburg, Germany, *E. Umbach,* Forschungszentrum Karlsruhe, Germany, *U. Höfer*, Philipps University Marburg, Germany

The injection of charge carriers at a molecule-metal interface plays a decisive role in the performance of organic semiconductor devices. Especially new electronic states that may develop due to the interaction of the adsorbed molecules with the metal substrate can alter the injection mechanisms drastically. We present a recent study for a well characterized model system of epitaxial 3,4,9,10-perylene tetracarboxylic acid dianhydride (PTCDA) thin films on a Ag(111) substrate. Two-photon photoemission (2PPE) displays a dispersing unoccupied state between the metallic Fermi level and the lowest unoccupied molecular orbitals (LUMO) of PTCDA with an effective electron mass of 0.39 $m_e$ at the Γ-point. Its energetic position in the band gaps of both the Ag(111) substrate and the PTCDA overlayer identify it as a genuine interface state, a result that is corroborated by model calculations. Time-resolved measurements show that the lifetime of electrons excited into this interface state is 55 fs. This is a relatively small value for an unoccupied state located only 0.6 eV above the Fermi level and is indicative for a large penetration of the wavefunction into the projected sp-gap of Ag(111). In order to investigate the role of the interface state for carrier transport between the organic semiconductor and the metal we populate the LUMO of PTCDA by absorbing 2.4 eV photons in films of varying thickness up to 100 ML and simultaneously record fluorescence and angle-resolved photoemission spectra. We observe a long lived component in the 2PPE intensity close to the Fermi level which clearly correlates with film thickness and fluorescence lifetime.

2:00pm **SS2-WeA2 Electronic Structure and Charge Separation at a Planar Molecular Heterojunction Probed by Two-Photon Photoemission**, ***G. Dutton***, *D.B. Dougherty, S.W. Robey,* National Institute of Standards and Technology, *W. Jin, W.G. Cullen, J.E. Reutt-Robey*, University of Maryland, College Park

The molecular donor-acceptor interface performs a critical function in the operation of organic photovoltaics as the sole site of charge separation. Understanding the electronic structure and exciton/polaron dynamics at these interfaces is crucial for developing the understanding of the relevant diffusion, dissociation and recombination processes necessary for achieving enhanced efficiencies. We have employed photoemission techniques, primarily two-photon photoemission spectroscopy (2PPE) and time-resolved pump-probe measurements, to examine these issues for thin organic films and heterointerfaces of pentacene and copper phthalocyanine with C60 fullerene. This talk will concentrate on results for interfaces between copper phthalocyanine and C60 formed on Ag(111). Using a combination of visible 1.75eV pump, corresponding to the phthalocyanine Q-band absorption maximum, and 5.25eV UV probe, we observe the ultrafast population dynamics of the C60 LUMO electron-polaron at 0.3 eV above the Fermi level. Preliminary analogies of corresponding physical molecular structures at this interface will also be presented based on STM results for the similar zinc phthalocyanine:C60 interface.

2:20pm **SS2-WeA3 Quantitative Three-dimensional Spin-Polarimetry in ARPES**, ***J. Osterwalder***, University of Zurich, Switzerland, *H. Dil, F. Meier,* University of Zurich and Paul-Scherrer-Institut, Switzerland, *J. Lobo,* University of Basel, Switzerland, *L. Patthey*, Paul-Scherrer-Institut, Switzerland **INVITED**

An angle-resolved photoelectron spectrometer has been equipped with a full three-dimensional spin polarimeter by using two orthogonal Mott detectors.[1] The unique capability of the instrument has made it possible to introduce a new two-step fitting routine that provides absolute spin polarization vectors for each individual band intersected in a particular ARPES spectrum or momentum distribution curve.[2] This procedure is crucial when analyzing strongly overlapping peaks or weak signals sitting on a large unpolarized background. It is robust against strong intensity variations due to matrix element effects because it references the spin polarization contribution of each band to the measured peak intensity. The method is applied to two-dimensional systems where spin-orbit effects lead to complex momentum-dependent spin structures.[3] Two prototypical systems, Bi/Ag(111) (√3x√3)R30° and Pb/Ag(111) (√3x√3)R30° were investigated. We confirm that the surface states experience a large spin splitting. Moreover, we find that all surface states are 100% spin polarized, and that for some states, spin polarization vectors rotate out of the surface plane. With the photoelectron spin as an additional tag in the measurement, spin-split bands with splittings far below the measured line width can be resolved. This has allowed us to see such splittings in quantum well states within ultrathin Pb layers on Si(111). Comparable to surface states, the space inversion symmetry is broken in these films, and the spin degeneracy of the valence electrons is lifted. The effect is much smaller though, and we measure energy splittings as small as 15 meV.

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### 3:00pm **SS2-WeA5 A New Spin on Chirality: Reactions Induced by Polarized Secondary Electrons from a Magnetic Substrate[1]**, ***R.A. Rosenberg***, *M.J. Abu Haija*, Argonne National Laboratory, *P.J. Ryan*, MUCAT, Ames Laboratory

Since nearly all biological compounds are homochiral, any model of the origin of life must be able to incorporate a mechanism that could lead to preferential chirality. Since chiral molecules have a certain handedness, many researchers have investigated the possible influence of circularly polarized UV photons and longitudinal spin-polarized electrons in creating an enantiomeric excess.[2-4] However, in general the demonstrated effects have been small and/or on the order of the experimental error. In the present work we hypothesize that a previously unappreciated source may play a role in chiral-selective chemistry: low-energy (0-20 eV) spin-polarized secondary electrons, produced by photon,[5] electron,[6] or ion[7] irradiation of a magnetic substrate. To test this theory we have performed detailed x-ray photoelectron spectroscopy measurements of the reaction rate for x-ray induced, secondary electron photolysis of a model chiral compound, R- or S-2-Butanol, adsorbed on a magnetized permalloy ($Fe_{0.2}Ni_{0.8}$) substrate. Our results show an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chiraltiy of the molecule and the spin polarization of the secondary electrons. Not only do our results demonstrate a chirality enhancement well above that of most previous work, but, since this mechanism only requires a magnetic substrate and ionizing radiation, it should be viable in a wide variety of possible prebiotic environments.

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### 4:00pm **SS2-WeA8 The Temperature-Dependent Dynamic Solvation of Excess Electrons at the 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide/Ag(111) Interface**, ***M.L. Strader***, Max Planck Institut für Metallforschung, Germany

Interest in room temperature ionic liquids (RTIL's) has increased rapidly in the last decade, fueled by the potential of RTIL's as environmentally friendly 'designer solvents'. The unusual, highly ionic character of RTIL's has motivated study of their fundamental physical properties. The dynamic solvation responses of various RTIL's have been studied in bulk, and extension of study to the interface could prove useful to electrochemical applications. Two-color, angle-resolved, two-photon photoemission (AR-2PPE) has been used to study interfacial solvation dynamics in ultrahigh vacuum (UHV) for a number of systems. Thin films of 1-butyl-1-methylpyrrolidinium bis(trifluoromethylsulfonyl)imide were epitaxially grown on Ag(111) and studied with AR-2PPE. The well-known low vapor pressures of RTIL's afford the rare opportunity to study interfacial solvation dynamics at electrochemically relevant temperatures in the liquid phase. A pronounced increase in solvation at elevated temperatures is observed.

### 4:20pm **SS2-WeA9 Novel Acoustic Plasmons on Metal Surfaces**, ***K. Pohl***, *B. Diaconescu*, University of New Hampshire, *G. Vercelli, L. Vattuone, M. Rocca*, CNISM, IMEM-CNR and Università di Genova, Italy

The recent discovery of a fundamentally new sound-like plasmon on a bare metal surface of beryllium may introduce a new research direction in the area of plasmonics.[1] While conventional surface plasmons are optical modes and have a finite excitation energy of a few eV, the novel acoustic mode can be excited with very low energies of a few meV. This allows, in principle, for a coupling with visible light for signal processing and advanced microscopies as well as new catalysts on metallic surfaces. In order to show that this novel excitation is a general phenomenon on closed-packed noble metal surfaces, as predicted by our theoretical collaborators,[2] we have measured the dispersion of the acoustic surface plasmon on Cu(111) by electron energy-loss spectroscopy for a parallel momentum-transfer range from 0 to 0.20 1/Å. We can report that the dispersion is indeed linear (acoustic) with a slope (sound velocity) in good agreement with theory,[2] and energy values that extend up to 1 eV. We will shown that the novel acoustic surface plasmon, ASP, is a general phenomenon on metal surfaces that support a partially occupied surface state within a wide bulk energy gap. It is caused by the non-local screening of the surface electrons due to bulk electron. The adsorption of about 0.25 ML of oxygen on the surface removes the surface state on Cu(111) and indeed destroys the ASP.

This work was supported in parts by the NSF under Grant No. DMR-0134933 and DMR-0753467, by the visiting scholar program of CNISM and by Compagnia S. Paolo.

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### 4:40pm **SS2-WeA10 Exploring Adsorption through Surface Resistivity Measurements**, *C. Liu*, ***R.G. Tobin***, Tufts University

Surface resistivity – the increase in the electrical resistivity of a thin metal film due to surface defects or impurities – is a simple and readily measured property that provides a window into complex nonequilibrium surface processes. It originates in the diffuse scattering of the metal's conduction electrons by the localized potential created by the surface modification, and depends in complicated fashion on the local electronic structure of the scatterer. The variation of surface resistivity with coverage, for both single adsorbates and coadsorption systems, gives insight into the effects of surface defects and neighboring adsorbates on the electron-scattering probability. We report on several surface resistivity studies that reveal different aspects of adsorption. All are carried out on 50 nm thick epitaxial Cu(100) films grown on H-terminated Si(100) substrates. CO adsorption on these films exhibits striking differences in electron-scattering cross section for adsorption on different sites, with CO on defect sites exhibiting near-zero net scattering.[1] Studies of oxygen and sulfur adsorption reveal the effects of interadsorbate interactions. Individually adsorbed oxygen and sulfur show very different coverage-dependences, with oxygen atoms acting as independent non-interacting scatterers while at high coverages sulfur strongly suppresses scattering by nearby sulfur atoms.[2] Sulfur has a similar effect on coadsorbed oxygen, reducing its effective scattering cross-section essentially to zero when the two atoms are adsorbed on adjacent lattice sites.[3] We suspect that the apparently zero differential resistivity observed for defect-bonded CO and for adsorption of O or S near a pre-adsorbed sulfur atom results not from zero electron scattering by the added adsorbate but from cancellation of the new adsorbate's added scattering by a reduction in scattering from the defect site or preadsorbed sulfur. These results can be analyzed qualitatively in terms of the behavior of adsorbate-derived orbitals near the Fermi level.

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### 5:00pm **SS2-WeA11 Dependence of Surface Properties on Adsorbate-Substrate Distance: Work Function Changes and Binding Energy Shifts for I/Pt(111)**, ***P.S. Bagus***, University of North Texas, *Ch. Wöll*, Ruhr Universität Bochum, Germany, *A. Wieckowski*, University of Illinois at Urbana-Champagne

A detailed analysis of the character of the bond of I adsorbed at on-top and three-fold sites of Pt(111) is presented. At both sites, the bonding is dominated by an ionic interaction supplemented with some covalent character due to donation from the adsorbed I anion to Pt. The way in which the I-Pt interaction affects observed properties, including the anomalous work function changes induced by the adsorption of I and the shifts of I core level binding energies, will be described. The surprising fact that a negatively charged adsorbate leads to a work function decrease, rather than the increase expected solely due to the charge of the adsorbate, arises from electronic reorganizations that cancel the dipole due to the charged adsorbate.[1] Furthermore, the contributions that lead toward an interface dipole that lowers the work function are larger as the adsorbate moves closer to the surface. Thus, the magnitude of the change in the interface dipole can be directly correlated with the distance of the I adsorbate from the Pt surface. A similar distance dependence is also found for the shifts of the I core level binding energies. In effect, these shifts can be interpreted to indicate adsorbate height. In particular, the shifts provide a new way to distinguish I adsorption at on-top and three-fold sites of Pt(111) since the distance of I from Pt(111) is different for these two sites. Furthermore, the effects important for the shifts of the interface dipole in the simpler case of I/Pt are also relevant for the charge transport barrier between a metal substrate and an organic adsorbate.[2] Thus the distance dependence demonstrated here for I/Pt may also provide information helpful for understanding these more complex systems.

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5:20pm **SS2-WeA12 Influence of Quantum Well States on Apparent Tunneling Barrier Height in Ultra Thin Pb Films**, ***J.D. Kim***, *S.Y. Qin*, *C.K. Shih*, The University of Texas at Austin

The thickness dependence of tunneling decay constant (κ) for ultra thin Pb films is studied with various sample biases by using low temperature STM. It is found that quantum well states (QWS) have a strong influence on κ. While the decay constant versus layer thickness (κ vs. L) clearly shows bilayer oscillations, we found that the apparent contrast in κ vs. L also show strong bias dependence. This result shows that κ-oscillation does not necessarily imply the work function oscillation. We further show that in this case, the parallel component of crystal momentum plays a critical role in tunneling process and is largely responsible for the observed phenomena. On the other hand, at large negative sample bias, the measured decay constants shows less bias dependent. Nevertheless, at small negative biases (less than 0.3 V below), the measured κ is strongly influenced by location of QWS near Fermi energy.

1NSF-IGERT DGE-0549417; NSF-FRG 26-1126-8750.

## Thin Film
## Room: 302 - Session TF-WeA

## Computational and Experimental Studies of Thin Films
## Moderator: S. Gupta, The Ohio State University

2:00pm **TF-WeA2 Phase Evolution in Sputter Deposited Hafnia-Titania Nanolaminates with Changing Architecture and Thermal Annealing**, ***M.C. Cisneros-Morales***, *C.R. Aita*, University of Wisconsin-Milwaukee

Thin film $HfO_2$ is a candidate for a high dielectric constant replacement material for $SiO_2$ in integrated circuits. The addition of $TiO_2$ to $HfO_2$ has shown promise for producing a $Hf_{1-x}Ti_xO_2$ ternary with an even higher dielectric constant than pure $HfO_2$ while maintaining thermal stability with Si. A convenient way of combining $TiO_2$ with $HfO_2$ in thin films is to sequentially sputter deposit them in a nanolaminate structure. In such a structure, interfaces are important in determining phase composition. The bulk pseudobinary $HfO_2$-$TiO_2$ temperature-composition phase diagram shows low miscibility between the end-point oxides. In this respect, the $HfO_2$-$TiO_2$ system is typical of an oxide nanolaminate in which there is a driving force for the formation of an interfacial mixed cation compound but there is no obvious kinetic path to achieve this structure via the formation of an interfacial crystalline substitutional solid solution. In this paper we examine the moderate temperature annealing behavior of $HfO_2$-$TiO_2$ nanolaminates with many different bilayer architectures. Multilayer stacks of $HfO_2$ and $TiO_2$ bilayers were grown on unheated fused silica substrates in a rf-excited multiple cathode reactor. The substrates were sequentially positioned under Hf and Ti targets and sputtered in 20 mtorr 80% Ar-20% $O_2$ discharges to build up the films. Four sequential annealing stages were carried out in laboratory air at the following temperatures: (I) 573 K, (II) 673 K, (III) 773 K, (IV) 973 K for 1 h each. The films were furnace cooled to room temperature and analyzed by double angle x-ray diffraction between annealing stages to obtain crystallographic data. The results show that the as-grown films are nanocrystalline and contain a mixed cation interface. This interface develops upon annealing into an orthorhombic $HfTiO_2$ phase adjacent to a titania layer, followed by an unusual metastable phase, monoclinic $Hf_{1-x}Ti_xO_2$ more remote from the interface. In nanolaminates with thicker $HfO_2$ layers, a simulaneous development of monoclinic $HfO_2$ occurs. The lattice parameters of this nanocrystalline intralayer phase, however, are greater than the expected bulk value, indicating dipole-dipole repulsion at the surface of a $HfO_2$ nanocrystal might be occurring.

2:20pm **TF-WeA3 Rapid Diffusion of Magic-Size Islands by Combined Glide and Vacancy Mechanism**, ***O.U. Uche***, *J.C. Hamilton*, Sandia National Laboratories

Monolayers of Ag on Cu(001) are well known to reconstruct forming a (10x2) reconstruction with Ag atoms packed hexagonally on the four-fold Cu(001) surface.[1] We have investigated the surface diffusion of hexagonally-packed Ag monolayer islands of various sizes on Cu(001) using computer simulation techniques. Our examination reveals a novel cooperative diffusion mechanism consisting of core glide coupled with the migration of edge vacancies. It should be noted that island diffusion is completely one-dimensional with the orientation determined by the (10x2) reconstruction of the diffusing island. In other words, rows of the hexagonal Ag lattice move along the hollow and bridge sites of the Cu substrate in the {110} type direction. In addition, we have observed magic-sized islands for which diffusion occurs much more rapidly as a result of their reduced diffusion barrier. In particular for a 169-atom hexagonal island, the activation energy for diffusion is smaller than the barrier for a single Ag atom hop. For this island size, diffusion occurs rapidly at temperatures as low as 200K. Molecular dynamics simulations suggest that the surface diffusion process displays non-Arrhenius behavior possibly resulting from the temperature-dependent lattice mismatch. Our findings should provide insight to future experimental research on the size distribution and shapes observed during the growth of thin films in similar systems.

[1] P.W. Palmberg and T.N. Rhodin, J. Chem. Phys. 49, 134 (1968).

2:40pm **TF-WeA4 The Influence of Oxygen Impurities on the Formation of Self-Assembled Nanostructures in Al/Al(110) Homoepitaxy**, ***Y. Tiwary***, *K.A. Fichthorn*, The Pennsylvania State University

Recent experimental studies of Al/Al(110) homoepitaxy show that self-assembled nano-structures can form due to an interplay between the kinetics of diffusion and deposition.[1] These “nanohuts” are characterized by smooth {111} and {100} facets. At temperatures between 330 and 500 K and for a deposition rate of 1 ML/min, the nanohuts emerge after about 10 ML have been deposited. Upon further deposition, these huts grow and self-organize, reaching average heights of 50 nm after 30 ML has been deposited. Understanding the formation of these features and developing the capability to control them in this and similar systems is both scientifically and technologically significant. To predict the formation and self-organization of these features, we employ first-principles calculations based on density-functional theory to study diffusion and atomic interactions on Al surfaces. We quantify many-body interactions between Al adatoms,[2] as well as the interactions between Al adatoms and isolated O impurities on Al(110). The interactions between Al and O atoms are expected to be especially important in the initial stages of growth, as oxygen is a common impurity on Al surfaces, even in ultra-high vacuum environments. We show that O impurities can significantly influence island nucleation and lead to entirely different growth modes than those observed in pure Al/Al(110) homoepitaxy. Using kinetic Monte Carlo, we simulate multi-layer growth under various conditions to predict the growth morphologies and understand the implications of surface impurities for self-assembled nanostructures.

[1] F. Buatier de Mongeot, W. Zhu, A. Molle, R. Buzio, C. Boragno, U. Valbusa, E. Wang, and Z. Zhang, Phys. Rev. Lett. 91, 016102 (2003).

[2] Y. Tiwary and K. A. Fichthorn, Phys. Rev. B 75, 235451 (2007).

3:00pm **TF-WeA5 A Formula for Increased Hardness and/or Ductility in TiN-based Thin Films and γ-TiAL Compounds**, *D.G. Sangiovanni*, ***V. Chirita***, *L. Hultman*, Linköping University, Sweden

TiN-based thin films, such as $Ti_{1-x}Al_xN$ and their alloys, are known to have excellent mechanical and thermal properties. In this paper we report the initial results of our ab-initio investigations of two novel ternary compounds, $Ti_{1-x}W_xN$ and $Ti_{1-x}Mo_xN$, obtained by alloying TiN with W, respectively Mo, in concentrations of up to 50%. The elastic constants as well as the bulk, shear and Young’s moduli of these compounds were evaluated using density functional theory calculations within the generalized gradient approximation, and compared with the corresponding properties of TiN and $Ti_{1-x}Al_xN$. Significantly, we found that the addition of W and Mo resulted in substantial increases in bulk modulus values compared to TiN (up to 15%) and $Ti_{1-x}Al_xN$ (up to 30%). At the same time, we observed a dramatic decrease (up to 50%) in the values of $C_{44}$, and a reversal of the Cauchy pressure, $C_{12}$-$C_{44}$, from negative to positive, results indicative of significantly increased ductility in these compounds. Both of these trends are in total contrast to what is known for $Ti_{1-x}Al_xN$, which exhibits increased $C_{44}$/brittleness and lower bulk modulus values as the Al content is increased. We also investigated, in the same manner, the effects of alloying $Ti_{0.5}Al_{0.5}N$ with W and Mo, in concentrations of up to 6% and observed a similar trend in increasing hardness and ductility. However, in the case of quarternary TiAl(W/Mo)N, the impact of W and Mo addition was considerably more moderate, as the increase in bulk modulus, respectively decrease in $C_{44}$, were in the 5% range. As it will be shown, these results demonstrate and help understanding the mechanisms through which W and/or Mo additions modify the atomic bonding in these compounds, from a strong angular/directional character, towards a more metallic type of bonding. This type of electronic structure information is essential in designing compounds with different mechanical properties and tailoring them to a variety of applications.

4:00pm **TF-WeA8 Ion Implantation and Annealing Studies on $VO_x$ Films Prepared by Pulsed dc Reactive Sputtering**, ***C. Venkatasubramanian***, *M.W. Horn*, *S. Ashok*, The Pennsylvania State University

Vanadium oxide ($VO_x$) thin films find extensive use in room-temperature bolometers for IR imaging. It is desirable to control and modify the electronic properties of the material with treatments such as ion implantation and thermal annealing. In this work, we report on the modification of structural and electrical properties of $VO_x$ thin films used in microbolometers. $VO_x$ films of varying compositions were deposited by pulsed dc reactive sputtering of a vanadium target under different oxygen flow rates. The as-deposited resistivities of the films ranged from 0.1 ohm-cm to 100 ohm-cm and the temperature coefficient of resistance (TCR) values varied from -1.1 to -2.7 % $K^{-1}$. $VO_x$ films used in microbolometer applications need to have a high TCR (> 2 % $K^{-1}$) and low resistivity values (1 -10 ohm-cm). But, typically, a high TCR is associated with a high resistivity. Hence ion-implantation followed by annealing was performed in order to examine trade-off between TCR and resistivity. Two species - Hydrogen (active) and Helium (inert) were chosen for implantation. Hydrogen is an active species well known for passivating defect states in a wide variety of electronic materials. Helium is an inert species and was chosen mainly to study the effects of bombardment on the film. The implanted films were annealed in an inert atmosphere to allow for redistribution of atoms, and then characterized by current-voltage measurements over a wide temperature range. The effect of thermal annealing alone was evaluated separately by annealing the unimplanted samples. In both cases, an order of magnitude change in resistance, and significant variations in TCR were observed. Further characterization has been done by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM) and transmission electron microscopy (TEM) to correlate these resistivity changes with the structure of the films.

4:20pm **TF-WeA9 Optical Properties and Structure of Magnetron Sputtered Vanadium Oxide Thin Films**, ***N.J. Podraza***, *B.D. Gauntt, N.M. Fieldhouse, K.E. Wells, D. Saint John, E.C. Dickey,* The Pennsylvania State University, *R.W. Collins,* University of Toledo, *M.W. Horn*, The Pennsylvania State University

Vanadium oxide ($VO_x$) thin films have been used for the last twenty years as the imaging material in uncooled infrared imaging devices. The important material properties for this application are a high thermal coefficient of resistance (TCR), controllable resistivity (ρ), low electrical noise and process compatibility with standard IC fabrication. In this work, device quality $VO_x$ thin films have been fabricated by single and dual-target pulsed dc magnetron sputtering. The deposition parameters of this novel technique include vanadium (V), vanadium dioxide ($VO_2$), or vanadium trioxide ($V_2O_3$) sputter targets which can be used individually or two targets simultaneously with separately variable power, variable total pressure, variable oxygen partial pressure, and variable substrate temperature. Variations in these parameters have been shown to result in films with TCR between 1.5 and 4.0 (-%/K ) and ρ ranging from 0.1-100,000 Ω cm as measured by a four-point probe technique. The films produced in the region of device interest have been characterized with a wide variety of ex situ techniques to establish what role the deposition parameters play in the final structure and composition of the film, and the resulting effects of these characteristics on the electronic transport and optical properties. Transmission Electron Microscopy (TEM), Rutherford Backscattering (RBS), and Spectroscopic Ellipsometry (SE) have been used to characterize the nanocrystalline structure of these films, their bonding structure, the oxygen content in the film, and the dielectric function spectra ($\varepsilon = \varepsilon_1 + \varepsilon_2$) in the visible range (0.75-6.5 eV), respectively. By utilizing these complementary techniques, correlations between changes in the microstructure and composition determined by TEM and RBS, optical properties determined by SE, and electronic transport properties have been established.

4:40pm **TF-WeA10 Multi-Scale Modeling of Thin-Film Epitaxy**, ***K.A. Fichthorn***, Penn State University **INVITED**

Predicting, with first-principles accuracy, the nanostructures that form during thin-film epitaxy is a current challenge in multi-scale modeling. I will discuss our recent innovations in accelerated molecular dynamics and coarse-grained lattice techniques, which facilitate this task. I will highlight these methods in studies aimed at understanding the morphology in Al(110) homoepitaxy. This system exhibits a number of interesting growth modes as the temperature and deposition rate are varied, including the formation of nanohuts. The nanohuts, which have smooth (111) and (100) facets, arise from a sea of smaller mounds after several layers are deposited, in a bimodal growth mode. We illustrate how first-principles total-energy calculations with density-functional theory, accelerated (ab initio) molecular dynamics, and kinetic Monte Carlo can be extended to yield insight into diffusion, many-body interactions, and growth in this system. I will illustrate the role of oxygen impurities in promoting bimodal growth.

## 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.

[1] Dietzel 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 thermomechnical 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 um) 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. Eggimand, 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.

# Wednesday Afternoon, October 22, 2008

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-WeA

## Exhibitor Workshops
**Moderator:** R.A. Childs, MIT

3:20pm **EW-WeA1 The What, Why and How of Self-Assembly of Alkanethiols: A Practical Tutorial*,* *D.J. Graham***, Asemblon Inc.

Alkanethiols are used in an ever increasing number of applications throughout a wide range of fields. These applications span from simple control of surface chemistry to the elaborate dreams of nanotechnology. Almost equal to the variety of their uses are the methods employed to create alkanethiol SAMs. This presentation will provide an overview tutorial of practical information on how to use alkanethiols to create homogenous, mixed, and patterned SAMs using methods such as solution assembly, microcontact printing, and other patterning methods. Learn about the what, why and how of using alkanethiols and avoiding some of the common pitfalls of creating SAM surfaces.

3:40pm **EW-WeA2 Real Time Film Thickness Monitoring on Roll to Roll Coaters*,* *E. Teboul***, HORIBA - Jobin Yvon Inc.

Flexible substrates have been increasingly used to support deposition of thin films for packaging, pharmaceutical and solar industries where cost efficient production and consistent quality coatings are the drivers. Real time thickness monitoring of the deposited layers present several challenges such as mechanical alignment, unrolling speed of the substrate and complex material properties of the substrate, that need to be overcome in order to perform a successful measurement. HORIBA Jobin Yvon has developed an in-line configuration of its UVISEL spectroscopic ellipsometer that address the measurements difficulties encountered on a roll to roll coater. The UVISEL is capable of measuring a spectral range from 190 nm to 880 nm in just fifty milliseconds (50 ms) that makes it suitable for most rolling speed currently used. New fitting algorithms have been developed in order to characterize accurately complex substrate materials. Example of real time dielectric film thickness and optical constants deposited on moving Polyethylene Terephthalate (PET) and Aluminum (Al) flexible substrates are presented.

## 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. Sanii, 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 elf-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 deals 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 lead to microscale pattens 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 insitu 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-hydorxyethyl)-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 um range. Mechanical testing results indicated a elongation of 620+/-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.

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11:40am **BI+NC-ThM12 Patterning of Plasma Polymers for Bioarray**, ***G. Mishra***, *S.L. McArthur*, University of Sheffield, UK

The high-density, multi-anaylate 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 AlGaN/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

AlGaN/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 AlGaN/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 AlGaN surface layer induced by the 2DEG. Any slight changes in the ambient of the AlGaN/GaN HEMT affect the surface charges of the AlGaN/GaN HEMT. These changes in the surface charge are transduced into a change in the concentration of the 2DEG in the AlGaN/GaN HEMTs. We have demonstrated AlGaN/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 AlGaN/GaN HEMT to detect glucose in the breath condensate. This approach makes a possibility of integrating AlGaN/GaN HEMT based sensors with ZnO nanorod sensors on a single "smart sensor chip" with the techniques of selective area functionalization and mircofluidic 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 Magnetic Tweezer Sensor for Ensemble Binding Events of Nonmagnetic Particles**, ***R.M. Erb***, *R.E. Ducker, S. Zauscher, B.B. Yellen*, Duke University

9:00am **BO+EM+BI+NC-ThM4 The Effect of Cell Culture Parameters on Cell Release Kinetics from pNIPAM**, ***H.E. Canavan***, University of New Mexico

9:20am **BO+EM+BI+NC-ThM5 Fabrication And Sample Preparation For Microfluidic Molecular Diagnostics**, ***C.M. Klapperich***, Boston University **INVITED**

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. Teplyakov*, 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-modied 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 spectroscopy (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 the 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. Prauzner-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 Funtionalized Fullerenes on a Closed Packed Metal Surface**, ***B. Diaconescu***, University of New Hampshire, *T. Yang, S. Berber,* Michigan State University, *M. Jazdzyk, 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.

[*] This work was supported by the Nanoscale Science and Engineering Center for High-rate Nanomanufacturing (NSF NSEC-425826). Partial support has been provided by the NSF-NIRT grant ECS-0506309."

## Electronic Materials and Processing
## Room: 210 - Session EM+NC-ThM

## Contacts, Interfaces, and Defects in Semiconductors
**Moderator:** F. Ren, University of Florida

8:40am **EM+NC-ThM3 Point-probe Tunneling Measurements of Sheet Conductance of Metallized Silicon Surfaces**, ***H. Won***, *R.F. Willis*, The Pennsylvania State University

We report measurements of the sheet conductance of Si(111) 7x7 reconstructed surface and its metallization with Ag-overlayer. The experiment employs a STM-tip point tunneling probe coupled to a second spring-contact electrode to evaluate charge-carrier injection and transport via surface states prepared in-situ in UHV. The measurements distinguish a surface-states contribution, a Schottky diode contribution, and a metallic-overlayers dependence on thickness, ranging from submonolayer coverage to 10 monolayers. The thin film conductance shows a dependence on the interface conductance of the semiconductor, which is a function of the surface electron density.

9:00am **EM+NC-ThM4 Photoluminescece Spectroscopy on Near Surface InAs Quantum Dots and Wetting Layers**, ***I. Kamiya***, *K. Fukui*, Toyota Technological Institute, Japan

The electronic and optical properties of self-assembled (SA) InAs quantum dots (QDs) prepared by MBE or MOCVD have been one of the key topics of quantum nanostructures during the past few decades. In contrast to colloidal quantum dots such as CdSe with tri-octylphosphine oxide where the ligands plays a major role in passivating the surface,[1] SA InAs QDs are usually investigated without much concern on their surface/interface properties. However, we have shown that capping on the InAs QDs strongly influence their photoluminescence (PL)[2] or that the conductivity of surface InAs QDs strongly depends on their size.[3] More recently, it has been shown that surface and near surface InAs QDs exhibit features different from those of the well-buried.[4] Here, we have performed PL and PL excitation (PLE) spectroscopies on near surface InAs QDs and wetting layer (WL) to further investigate the influence of surface and interfaces of such structures. While we observed PL features similar to those reported in ref. 4, we have also found those that are different. PL and PLE measurements reveal that the carrier dynamics are stongly influenced by the surfaces and interface structures of the QDs and WL. We will discuss the mechanisms that could be governing such observations.

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9:20am **EM+NC-ThM5 Barrier Formation and Transport in Metal Contacts to Nanotubes and Nanowires**, ***A. Talin***, *F. Leonard, B.S. Swartzentruber*, Sandia National Laboratories **INVITED**

The technology of metal-semiconductor contacts has progressed tremendously over the past fifty years. However, as device dimensions shrink well below 100 nm, and as new materials with novel composition and geometry are explored for 'next generation' electronic components, the underlying physics of metal-semiconductor contacts departs substantially from the early models of Schottky, Mott, and Bardeen. Single wall carbon nanotubes, for example, have a quasi-one-dimensional density of states and a relatively inert surface which results in less Fermi level pinning and a strong dependence of the contact barrier height on the metal workfunction. Nevertheless, the simple Schottky model fails to correctly predict the barrier height dependence on the nanotube band gap. The Schottky model is also inadequate for describing metal-nanowire contacts, even in the absence of strong one dimensional character in the band structure. In my talk, I will review recent experimental results for metal contacts to nanotubes and nanowires, and discuss how the dimensions and geometry of these nanostructures affect barrier formation. I will also discuss situations where bulk-limited transport in nanowires leads to non-linear current-voltage characteristics, and which is often, incorrectly, ascribed to contact effects.

10:40am **EM+NC-ThM9 Reliability of III-N Electronic Devices**, ***M. Shur***, Rensselaer Polytechnic Institute **INVITED**

III-N materials system has a much larger dislocation and defect densities than more conventional semiconductors, such as silicon or III-V materials, and III-N field effect transistors operate at much higher voltages and/or current densities. As a consequence, device reliability is one of major concerns for III-N semiconductor technology. In GaN-based field effect transistors, reliability mechanisms are linked to hot electron trapping, trap creation in high electric fields at the gate edges (especially at the gate edge closer to the drain), and to the gate leakage current. The electric field activated carrier trapping in the gate-to-drain spacing of AlGaN/GaN HFET is primarily responsible for the current reduction at RF frequencies (so-called current collapse, or RF dispersion. The defect states creation at the gate edges and in the drain-to-gate spacing depends on the device temperature. At relatively low temperatures, these defect states are created due to impurity anneal. At higher temperatures, crack and dislocation creation becomes the dominant mechanism leading to the permanent device failure. As a consequence, an extrapolation of high temperature accelerated reliability tests to lower temperatures might be inaccurate. Except for the failure mechanism related to the gate leakage current, other failure and performance degradation mechanisms are related to a high electric field at the drain edge of the device channel and in the drain-to-gate spacing adjacent to the gate. (Therefore, GaN-based RF switches operating at zero DC drain bias and having insulated gate structure (MOSHFETs and MISHFETs) do not have reliability problems.) Field plates and dual field plates diminish the maximum electric field in the device channel improving reliability. Another approach, still to be explored, is based on using Field Controlled Electrode at the drain, which a kind of a field plate attached to the drain, rather than to the gate or source. Leaky passivation helps discharging the trapped charge diminishing the current collapse. Optimization of buffer doping also improves reliability. These design approaches, using better quality substrates, and improving materials quality of III-N epitaxial films will allow to achieve long life times and stable performance for high power and high frequency GaN-based field effect transistors.

11:20am **EM+NC-ThM11 The SiC Surface: A Surface of Growing Technological Importance**, ***C.R. Eddy, Jr.***, *D.K. Gaskill, M.A. Mastro, R.T. Holm, B.L. VanMil, R.L. Myers-Ward, M.E. Twigg, Y.N. Picard*, U.S. Naval Research Laboratory, *P.G. Neudeck, A.J. Trunek, J.A. Powell*, NASA Glenn Research Center

Silicon carbide has become a highly versatile substrate providing a foundation for device technologies based on III-V nitrides, silicon carbide and graphene materials. In each of these systems, the starting silicon carbide surface plays a pivotal role in determining the properties and qualities of the material. The importance of surface orientation and preparation to each materials system will be discussed in terms of step morphology and contributions of extended defects in the substrate. For III-V nitride heteroepitaxy, basal plane SiC is preferred and surface morphology plays a critical role in the defectivity of films. Engineered SiC substrate surfaces are used to create localized regions of the surface with widely varying step densities including areas nearly free of surface steps. Experiments show that surface steps are directly responsible for extended defects in the heteroepitaxial layers. Nearly step-free surfaces are used to demonstrate drastically reduced extended defect concentrations ($\leq 10^7$ cm$^{-2}$) in GaN epilayers. In regard to SiC homoepitaxy, the key elements are the control of polytype deposition, the removal of surface imperfections arising from the substrate, and the reduction or elimination of extended defects arising from the substrate or during the epitaxial nucleation process. Substrates are prepared oriented slightly away from the basal plane to promote single polytype epitaxy and off-cut toward <11-20> to promote the smoothest films. Although modification of the surface is an unavoidable first step to epitaxy due to the reactive nature of hydrogen at growth temperatures near 1600°C, the best epitaxy occurs when the surface is controllably etched to remove unwanted polishing damage. And with the desire to fully exploit the properties of SiC for high power devices, it is necessary to initiate the epitaxy in such a way as to greatly reduce or eliminate extended defects. In the new field of graphene formation through sublimation of SiC surfaces, key elements are the removal of surface imperfections from the substrate and the control of surface properties, i.e., steps that may be used advantageously for specialized devices. Key aspects of surface properties and preparation will be discussed in terms of surface structure and extended defect intersection with the surface as characterized by atomic force microscopy, electron channeling contrast imaging, and transmission electron microscopy.

11:40am **EM+NC-ThM12 Investigation of Negative Electron Affinity in Hydrogen Complex Deactivated Surface of InP:Zn (100)**, ***M.D. Williams***, Clark Atlanta University

Ultraviolet photoemission spectroscopy is used to investigate the development of negative electron affinity at the surface of hydrogenated Zn doped InP (100). Hydrogen injected into the material electronically passivates the local carrier concentration. Reverse-biased anneals of the InP under ultra-high vacuum show a dramatic change in the work function of the material within a set annealing temperature range suggesting the establishment of negative electron affinity at the surface. The strength of the negative electron affinity is 1.08 eV for a reverse bias field strength of approximately 1875 V/m . This value is consistent with the deactivation energy of the H-Zn complex (1.14 eV) determined previously. Spectral features are also shown to be sensitive to sample temperature. Hydrogen retrapping at the surface limits the effect and it is dependent on surface conditions.

## 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 accepter-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-Universitat Erlangen-Nurnberg, 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 Trimetasphere® carbon nanomaterials (TMS). Trimetaspheres® are endohedral metallofullerenes that consist of a trimetal nitride cluster enclosed in a C80 cage. First-generation Trimetasphere® 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 heterojuncion 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 these 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 μA/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 pyrolitic 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 Wisonsin-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 $TiO_2$ 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 $TiO_2(110)$ and wurtzite ZnO single crystal surfaces to adsorption on more technologically relevant $TiO_2$ 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 $TiO_2(110)$ surface and that the N3 dye molecules can be imaged after sensitization. For N3 on $TiO_2(110)$ 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 $TiO_2$ 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 $TiO_2$. 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 $TiO_2$ electrode. Zinc oxide (ZnO) is a wide band gap semiconducting material with a similar band gap and electron affinity to those of $TiO_2$ 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 $SnO_2$:F coated glass by sol–gel technique with polyethylene glycol (PEG) as organic template, $Zn(CH_3COO)_2.2H_2O$ as precursor, ethanol as solvent and $NH(C_2H_2OH)2$ 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 $Zn(CH_3COO)_2$ 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 $Zn(CH_3COO)_2$ 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. Baricuatro*, 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.

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 incognito. 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).

## Magnetic Interfaces and Nanostructures
## Room: 206 - Session MI-ThM

## Magnetic Surfaces, Interfaces, Thin Films and Heterostructures
### **Moderator:** J. Shen, Oak Ridge National Laboratory

8:00am **MI-ThM1 Exchange-Split Surface State on Gd(0001) Revisited**, ***M. Budke***, *M. Donath*, WWU Münster, Germany

Gd is considered to be a prototype Heisenberg ferromagnet, because its magnetism originates from the strongly localized electrons in the half-filled f shell and is mediated via RKKY interaction by the conduction electrons. Close to the Fermi energy $E_F$ an exchange-split d-like surface state is found, which is thought to be responsible for peculiar magnetic effects of the Gd(0001) surface. The behaviour of this surface state close to Curie temperature $T_C$ has been controversially discussed: spin-resolved inverse photoemission (IPE) has identified a surface state with both, minority and majority components right above the Fermi energy $E_F$ already 10 years ago.[1] While the majority state shifts to higher energies upon approaching $T_C$ the minority state shifts to lower energies. This Stoner-like collapsing band behaviour is in contradiction to results from spin-resolved photoemission (PE), where the surface state shows up at 0.2 eV below $E_F$ and exhibits spin-mixing behaviour upon approaching $T_C$.[2] The present widely accepted picture of the surface state on Gd(0001) comprises a majority component 0.2 eV below $E_F$ and a minority component 0.4 eV above $E_F$ at low T. As identified by spin-integrated scanning tunneling spectroscopy[3] the exchange splitting slightly reduces with increasing T and remains 0.4 eV at $T_C$.[3] However, the unoccupied majority component as identified by IPE still remains mysterious. One reason for the conflicting results might be found in different sample conditions since the Gd films are usually grown on W(110), a material with considerably different lattice constant than Gd. To overcome this suspicion, we performed combined spin-resolved PE and IPE measurements on one and the same sample preparation of a 30 ML Gd film grown on Y(0001). We were able to identify two surface states with their minority and majority components well separated from $E_F$. While the occupied surface state shows spin-mixing behaviour as observed in other PE experiments, the unoccupied surface state exhibits an exchange splitting of 250 meV that vanishes at $T_C$.

[1] Donath et al., PRL 77, 5138 (1996).

[2] Li et al., Phys. Rev. B 51, 13895 (1995).

[3] Getzlaff et al., JMMM 184, 155 (1998).

8:20am **MI-ThM2 Electrical Injection and Detection of Spin-Polarized Carriers in Silicon in a Lateral Transport Geometry**, ***O.M.J. van 't Erve***, *A.T. Hanbicki, M. Holub, C.H. Li, C. Awo-Affouda, G. Kioseoglou, P.E. Thompson, B.T. Jonker*, Naval Research Laboratory

The electron's spin angular momentum is one of several alternative state variables under consideration on the International Technology Roadmap for Semiconductors for processing information in the fundamentally new ways, which will be required beyond end-of-roadmap CMOS technology. Electrical injection / transport of spin-polarized carriers is prerequisite for developing such an approach. Significant progress has recently been made on spin injection into the technologically important semiconductor, Si, using vertical device structures.[1,2] Here we present the electrical injection, detection and magnetic field modulation of lateral diffusive spin transport through silicon using $Fe/Al_2O_3$ surface contacts.[3] The $Fe/Al_2O_3$ tunnel barrier contacts are used to create and analyze the flow of pure spin current in a silicon transport channel. A nonlocal detection technique has been used to exclude spurious contributions from AMR and local Hall effects. The nonlocal signal shows that a spin current can be electrically detected after diffusive transport through the silicon transport channel and the signal depends on the relative orientation of the magnetization of the injecting and detecting contacts. Hanle effect measurements demonstrate that the spin current can be modulated by a perpendicular magnetic field, which causes the spin to precess and dephase in the channel during transport. The realization of efficient electrical injection and detection using tunnel barriers and a simple device geometry compatible with "back-end" Si processing should greatly facilitate development of Si-based spintronics. This work was supported by ONR and core NRL programs.

[1] Jonker et. al., Nat. Phys. 3, 542 (2007)

[2] Applebaum et. al., Nat. 447, 295 (2007) .

[3] van 't Erve et. al., Appl. Phys. Lett. 91, 212109 (2007).

8:40am **MI-ThM3 Room Temperature Ferromagnetism and Surface Morphology in Cr-doped $Ga_2Se_3$ Films on Si(001)**, ***E.N. Yitamben***, *T.C. Lovejoy*, University of Washington, *D.F. Paul, J.B. Callaghan*, Physical Electronics USA, *S.C. Fain, F.S. Ohuchi, M.A. Olmstead*, University of Washington

The intrinsic vacancy semiconductor $Ga_2Se_3$, which may be grown epitaxially on Si, presents several interesting issues for the study of dilute magnetic semiconductors. Transition metal doping may lead to occupation of either vacancy sites or Ga sites in the lattice, which could lead to n- or p-type doping, respectively. The vacancy-induced anisotropy and wide bandgap (2.3 eV) may also lead to high Curie temperatures. To probe the interaction between magnetism, morphology, and free carriers in this new class of magnetic material, experimental investigations of Cr-doped $Ga_2Se_3$ epitaxially grown on Si(100):As have been pursued. Inclusion of Cr into the $Ga_2Se_3$ lattice results in new states at the Fermi edge, signaling a metallic structure, and the films are ferromagnetic at room temperature (though with a saturation moment about 1/4 of the low temperature value.) Scanning tunneling microscopy reveals formation of clusters within trenches whose shape and size depend on the Cr concentration and whether or not an undoped $Ga_2Se_3$ buffer layer is deposited first. Scanning Auger microscopy reveals a compositional difference between the clusters and the terraces surrounding them, with a larger Cr:Ga ratio in the clusters. We suggest this concentration difference, and the resultant strain and/or difference in chemical potential, may control the size and shape of the trenches surrounding the clusters. Work supported by NSF grant DMR-0605601 and NER-0508216. ENY was supported by an IBM Fellowship; TCL was supported by an IGERT Fellowship, NSF/NCI DGE 0504573. Some experiments were performed at the Advanced Light Source, Berkeley, supported by DOE contract DE-AC02-05CH11231.

9:00am **MI-ThM4 Organic-based Magnetoelectronics from an Electronic Structure View**, ***A.N. Caruso***, U. of Missouri - Kansas City, *K.I. Pokhodnya*, North Dakota State U., *W.W. Shum*, U. of Utah, *W.-Y. Ching*, U. of Missouri - Kansas City, *B. Anderson, M.T. Bremer*, North Dakota State U., *E. Vescovo*, Brookhaven National Lab., *P. Rulis*, U. of Missouri - Kansas City, *A.J. Epstein*, Ohio State U., *J.S. Miller*, U. of Utah **INVITED**

Successful semiconductor magnetoelectronic device operation requires solids with the ability to inject and/or retain carrier spin polarization across multiple interfaces. Inorganic transition metal doped semiconductors (postulated dilute magnetic semiconductors such as Co:TiO2 and Mn:GaAs) have not been able to meet these criterion at room temperature due to solubility problems.[1] Organic-based magnets however, offer increased interfacial stability and elastic spin carrier lifetimes, due to the small differences between their surface and bulk free energies, and low spin-orbit scattering and/or hyperfine interactions.[2] The remaining piece is to directly show that organic-based magnets are indeed capable of electron spin polarization at or near the Fermi edge. The first direct evidence of an organic-based magnet with a finite electron spin polarization at the Fermi edge, collected from spin resolved photoemission of $[Fe^{II}(TCNE)(NCMe)_2][Fe_{III}Cl_4]$[3] will be presented. An ab initio calculation of the spin resolved band structure will also be presented, backing the claim that $[Fe^{II}(TCNE)(NCMe)_2][Fe_{III}Cl_4]$ is a half-semiconductor. Lastly, the electronic structure relationship between magnetic exchange and structural bonding will be discussed within the context of the experimental and computational results.

[1] A. R. Rocha, V. M. Garcia-Suarez, S. W. Bailey, C. J. Lambert, J. Ferrer, S. Sanvito, Nature Materials 4, 335 (2005).

[2] Satishchandra Ogale, Darshan Kundaliya, Shareghe Mehraeen, Lian-feng Fu, Shixiong Zhang, Alexandre Lussier, Joe Dvorak, Nigel Browning, Yves Idzerda, Thirumalai Venkatesan, Chem. Mater. 20, 1344 (2008).

[3] K. I. Pokhodnya, M. Bonner, J.-H. Her, P. W. Stephens, J. S. Miller, J. Amer. Chem. Soc. 128, 15592 (2006).

10:40am **MI-ThM9 Electrical Spin Injection into InAs Wetting Layer**, ***C.H. Li***, *G. Kioseoglou, A.T. Hanbicki, R. Goswami, C.S. Hellberg, B.T. Jonker*, Naval Research Laboratory, *M. Yasar, A. Petrou*, SUNY Buffalo

Efficient electrical injection of spin-polarized electrons from a magnetic contact into a semiconductor is an essential requirement for utilizing the spin degree of freedom in semiconductor spintronic devices. InAs is an attractive material for optoelectronic and high-speed transistor devices due to its small bandgap and high electron mobility. Owing to its large Rashba spin-orbit coupling, the 2-dimensional electron gas (2DEG) formed in InAs-based heterostructures has also been proposed for spin transport within a spin field effect transistor (FET).[1] Here we demonstrate efficient spin injection from Fe into a thin (~3ML) InAs wetting layer (WL) that forms on GaAs before the formation of InAs quantum dots (QDs).[2] Cross sectional scanning tunneling microscopy (STM) and transmission electron microscopy (TEM) show that the WL is continuous laterally over many microns, and that it is an intermixed InxGa1-xAs layer. Transport measurements reveal a 2DEG-like behavior. The WL electroluminescence is readily distinguished from that of the QDs, and dominates emission at higher biases over a wide temperature range up to RT. We measure an optical circular polarization of 26% at 5K due to the injection of spin-polarized electrons from a reverse-biased Fe Schottky contact, which corresponds to an electron spin polarization >50% after lifetime corrections, demonstrating that even this remarkably thin layer supports high spin polarization. This polarization stayed relatively constant up to 60K, and decreased to ~6% at room temperature, consistent with the D'yakonov-Perel spin relaxation mechanism which dominates at high temperatures.

Work at NRL are supported by ONR and NRL core funds. Work at SUNY are supported by NSF.

[1] S. Datta and B. Das, Appl. Phys. Lett. 56, 665 (1990).

[2] C. H. Li et al. APL 91, 262504 (2007).

11:00am **MI-ThM10 Phase Coexistence in the AF to FM Transition in Epitaxial FeRh Thin Films**, *D.A. Arena*, ***Y. Ding***, Brookhaven National Laboratory, *L.H. Lewis*, Northeastern University, *C.J. Kinane, B.J. Hickey, C.H. Marrows*, University of Leeds, UK, *J.-W. Kim, P.J. Ryan*, Argonne National Laboratory & Ames Laboratory, *M. Ali*, University of Leeds, UK

The near equiatomic, ordered alloy FeRh exhibits an unusual first order antiferromagnetic (AF) to ferromagnetic (FM) phase transition at around 380 K[1] and interest in this system has increased recently, driven both from unresolved scientific questions and potential applications in high-density storage media and advanced sensors. In these studies, highly ordered, epitaxial thin films of FeRh, grown by molecular beam epitaxy (MBE), were measured with a variety of techniques including using x-ray magnetic circular dichroism (XMCD), and conventional and surface x-ray diffraction (XRD). XMCD was measured in two modes: surface sensitive total electron yield (TEY) and bulk sensitive indirect transmission (IT). The TEY data reveal a persistence of ferromagnetism in the near surface region at room temperature while the indirect transmission data indicate that the bulk material is not FM ordered and is presumably AF. In general terms, conventional XRD measurements from our thin films show that the AF to FM phase transition, which is hysteretic in temperature, is accompanied by an abrupt lattice expansion; this behavior mirrors the expansion observed in bulk samples. However, high-resolution XRD data indicate that the lattice expansion is not smooth, but rather occurs via the coexistence of two distinct lattice parameters, where the smaller volume lattice is presumably associated with the AF phase and the larger lattice contains the FM ordered FeRh. Surface XRD, acquired near the critical angle for x-ray penetration, reveals that the temperature for the transition from the smaller to the larger lattice parameter occurs at a reduced temperature for the surface than for the bulk. Comparisons with the XMCD data for different capping layers of the FeRh films and sum-rule analyses of the Fe magnetic moment will also be discussed.

[1] J. S. Kouvel and C. C. Hartelius, J. Appl. Phys. 33, 1343 (1962).

11:20am **MI-ThM11 A Surface-Driven Route to the Synthesis of Mn-Si and Mn-Ge-Quantum Dot Nanostructures**, ***C.A. Nolph***, *H. Liu, P. Reinke*, University of Virginia

The combination of the group IV semiconductors silicon and germanium with an element with a large magnetic moment, such as Manganese, is a critical step in the development of novel and versatile spintronics devices. The goal of our studies are to firstly, incorporate Mn as delta-doped layers in a crystalline Si matrix, which is predicted to present a ferromagnetic structure with a half-metallic character, and secondly, to magnetically dope Ge-quantum dots, which are fabricated by a strain-driven Stranski-Krastanov growth on a Si(100) surface. The synthesis of both types of nanostructures begins with the deposition of Mn on a Si(100)-2x1 surface, which serves as the template for the subsequent Si or Ge overlayer growth. The evolution of nanostructures is observed with scanning tunneling microscopy (STM), and photoelectron spectroscopy (PES) to study bonding and electronic structure at the surface. The prerequisite for a successful synthesis of the Mn-doped Si and Ge nanostructures is to control the Mn-surface structure on Si(100)-(2x1), which is achieved by establishing the surface phase diagram as a function of temperature and Mn-coverage. At room temperature the formation of short monoatomic Mn wires, oriented perpendicular to the Si-dimer rows, dominates. Upon heating the Mn-adatom wires are first transformed to subsurface Mn-Si then the formation of Mn-silicide crystallites occurs. At the same time, the defect density on the Si surface rises dramatically, including a loss of structural integrity at the terrace edges. The surface phase diagram establishes guidelines for the subsequent formation of Si-overlayers and Ge QD growth, and shows the variability in Mn-surface structures and bonding within the Mn-Si(100)-(2x1) system; the consideration of these factors will decisevely influence the resultant magnetism of Mn-delta doped Si-structures. A first assessment of the magnetism in the layered structure is obtained from a measurement of the anomalous Hall-effect contribution to transport and will be discussed. The deposition of Ge was explored in the low temperature and mobility regime and the Mn-nanostructure remains indeed unperturbed by the growth of the Ge-overlayer. After the room-temperature deposition of a thin Ge buffer layer in order to contain and protect the Mn-nanostructure, the transition is made to conditions which allow the formation of Ge quantum dots, and presumably will allow the Mn to move into the QD from the Si-Ge interface.

11:40am **MI-ThM12 Magnetic Exchange Bias in Epitaxial $Fe_{25}Pt_{75}$**, ***G.J. Mankey***, University of Alabama, *P. Mani*, Western Digital, *D. Lott*, GKSS Research Center, *F. Klose*, Australian Nuclear Science and Technology Organisation, *H. Ambaye*, Oak Ridge National Laboratory, *M. Wolff*, Ruhr-University Bochum, Germany, *A. Schreyer*, GKSS Research Center, *H.M. Christen, B.C. Sales*, Oak Ridge National Laboratory, *M.J. Walock, Z. Lu, P. LeClair*, University of Alabama

Epitaxial films of $Fe_{25}Pt_{75}$ have a number of different magnetic phases as a function of temperature and chemical order. For example, chemically-ordered epitaxial films have two distinct antiferromagnetic phases at temperatures below ~160K, and exhibit paramagnetism above that temperature. In sharp contrast, chemically-disordered epitaxial films are ferromagnetic with a Curie temperature that is greater than 400K. Since both antiferromagnetic and ferromagnetic phases can exist in a partially-ordered film at temperatures below 160K, a magnetic exchange bias in the chemically-disordered ferromagnetic component can be induced through contact with the chemically-ordered antiferromagnetic component of the film. By varying the process conditions during growth, an alloy with the same composition throughout the film can exhibit a modulated magnetic structure. Using a combination of polarized neutron reflectivity and other magnetic characterization techniques, the observed exchange bias in such films is demonstrated to originate at the interfaces between the ferromagnetic and antiferromagnetic phases of $Fe_{25}Pt_{75}$.

## 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 advantegous. 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/$SiO_2$ 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 $cm^2/Vs$ for Pn and 0.04 $cm^2/Vs$ for P3HT. Bottom-gate CNTM TFTs exhibited p-type behavior, mobilities of 13.7 $cm^2/Vs$, on/off ratio of $10^3$ and minimal hysteresis. Top-gate graphene TFTs exhibited mobilities of $1.0x10^4$ $cm^2/Vs$ for holes and $4x10^3$ $cm^2/Vs$ 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 Lipshitz 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.

11:40am **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 $C_4F_8$/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. Räisänen,* 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.; Räisänen, 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 opto-electronics 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 $140<L<547$nm and dwell time $200<t<1600$ microseconds results in well defined arrays of nanometer deep holes. The diameter ($20<d<60$nm) and depth ($0.7<z<4.4$nm) 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.

[2] Basu, R., et al., Langmuir, 2007. 23(4): p. 1905-1911.

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 heirarchy 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 ($CH_3$) and amino ($NH_3^+$)-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 $NH_3^+$ 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.

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[2] H.-C. Kwon et al., J. Phys. Chem. B 109, 10213 (2005).

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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 $Zn^{2+}$.[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.

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[2] K. Enander, G. T. Dolphin, L. Baltzer, J. Am. Chem. Soc. 2004, 126, 4464.

10:40am **NS+NC-ThM9 Non-IPR $C_{60}$ 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 $C_{60}$ isomers (IPR = Isolated Pentagon Rule) have been generated by depositing vibronically excited $C_{60}$ ions on HOPG and subsequently sublimating the undesired IPR $C_{60}(I_h)$ 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 $C_{60}$ 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 $C_{60}$ cages. The relative amount of these S-W isomers, $C_{60}$ (S-W), deposited from the beam of hot $C_{60}$ ions scales with the kinetic energy of electrons used for excitation/ionization. Essentially pure $C_{60}$(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, $C_{60}(I_h)$. The topography of the resulting films, as studied by means of AFM, is governed by the aggregation of the $C_{60}$(S-W) cages and reflects intercage bonds constituted by non-IPR sites. These covalent intercage bonds are responsible for the higher stability of the $C_{60}$(S-W) films as mirrored by a sublimation offset at ~1100 K (compared to $C_{60}(I_h)$ which sublimes at ~ 550 K). In contrast to the characteristic doublet structure of the HOMO-derived band in $C_{60}$ $(I_h)$ films, the valence band of the $C_{60}$(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 $C_{60}$(S-W) films exhibit a narrower HOMO-LUMO gap than found for $C_{60}(I_h)$ 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.

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[2] N. Depalo et al., J. Phys. Chem B (2006), 110, 17388

[3] E. Sardella et al, Plasma Process. and Polym. (2006) 3, 456

[4] R. 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.

## Plasma Science and Technology
## Room: 304 - Session PS1-ThM

## Atmospheric Plasma Processing and Micro Plasmas
**Moderator:** J. Hopwood, Tufts University

8:00am **PS1-ThM1 Plasma Diagnostics in Microdischarges Using Laser Scattering**, ***S.G. Belostotskiy********, *V.M. Donnelly, D.J. Economou*, University of Houston, *N. Sadeghi*, Universite J. Fourier de Grenoble, France

Laser scattering experiments were performed in high pressure (100s of Torr) DC microdischarges operating in argon or nitrogen. Laser Thomson Scattering (LTS) and Rotational Raman Scattering were employed in a novel, backscattering, confocal configuration to measure important plasma parameters. LTS allows direct and simultaneous measurement of both electron density ($n_e$) and electron temperature ($T_e$). LTS experiments in microdischarges are challenging because of the low signal and excessive stray light. Measurements were performed at the center of the gap of a parallel plate slot-type microdischarge with plate separation of 600 microns. This location corresponded to the positive column of the DC microdischarge. For 50 mA current and over the pressure range of 300 – 700 Torr, measurements yielded $T_e = 0.9 \pm 0.3$ eV and $n_e = (6 \pm 3)\cdot 10^{13}$ $cm^{-3}$, in reasonable agreement with the predictions of a mathematical model. In order to obtain absolute values of the electron density, calibration of the Thomson scattered intensity was carried out using Raman scattering in nitrogen. This Rotational Raman spectroscopy was also employed to measure the gas temperature ($T_g$) in nitrogen DC microdischarges. Gas temperatures were determined by matching experimental spectra to synthetic spectra obtained by convolution of theoretical line intensities with the apparatus spectral resolution, with $T_g$ as the adjustable parameter. Measurements were performed for a set of $N_2$ pressures (P = 400 – 600 Torr) and over the current range of 5 – 30 mA. In the center of the interelectrode gap, $T_g$ changed from 450 ± 40 K at 5 mA to 740 ± 40 K at 30 mA. The gas temperature was nearly independent of pressure within the error of the experiment. Advantages and limitations of the laser scattering techniques employed will also be discussed.

8:20am **PS1-ThM2 The Effect of Excitation Frequency on Microplasmas**, ***J. Xue***********, *J. Hopwood*, Tufts University

In the microwave band, higher excitation frequency is found to enhance microplasma generation. The microplasma is formed by a split-ring resonator (SRR) consisting of a half-wavelength microstrip transmission line formed into a ring with a micromachined discharge gap.[1] The SRR plasma can be operated from 0.1 to 760 Torr with less than 0.5 W of power in He and Ar. Typically, microplasmas have been generated with DC, AC, RF, and microwave power. One unanswered fundamental question, however, concerns the effect of frequency on microplasma generation. The excitation frequency of capacitively coupled plasma has been discussed by Surendra and Graves.[2] This early work suggests that plasma density scales as the square of the applied excitation frequency. That work focused on large-scale plasma at low pressure and the excitation frequency was limited to less than 120 MHz. This paper presents plasma impedance analysis of three microplasmas operating at excitation frequencies of 450 MHz, 900 MHz, and 1.8 GHz. The electron density and sheath capacitance of the microdischarges are extracted from the plasma impedance. Experimentally, these three SRR's are fabricated on microwave laminate (Rogers, RT/Duroid 6010LM) with identical microstrip widths (1 mm) and discharge gaps (200 μm). The radii of the rings are scaled by 1/f and the smallest radius is 5mm at 1.8 GHz. To determine the plasma impedance, the microwave reflection coefficient is measured as a function of frequency while maintaining a constant microwave power absorbed by the plasma. Using the method in Ref. 1, the microplasma impedance is found by fitting the theoretical microwave reflection coefficient to the measured reflection coefficient. The results show that microplasmas generated by higher frequency resonators have a lower plasma resistance. The extracted electron densities in argon microplasma at 760 Torr are estimated as 2.4, 6.0, and $8x10^{13}$ $cm^{-3}$ for the 450 MHz, 900 MHz, and 1.8 GHz SRR, respectively. The imaginary part of the plasma impedance provides a model of the plasma sheath capacitance. This data shows a diminishing sheath impedance at high frequency which is responsible for improved electron density.

[1] F. Iza and J. Hopwood, Plasma Sources Sci. Technol. 14, 397 (2005).

[2] M. Surendra and D. B. Graves, Appl. Phys. Lett. 59, 2091 (1991).

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* PSTD Coburn-Winters Student Award Finalist

8:40am **PS1-ThM3 Generations, Characterizations and Applications of Microplasmas Operated in Atmospheric Gases and Artificial Media**, ***K. Tachibana***, Kyoto University, Japan **INVITED**

Microplasmas of sub-millimeter to micrometer scales can be operated in high pressure gases or high density media with a choice of single or integrated usage. The electron density $n_e$ of a typical microplasma lies in the range of $10^{12}$ to $10^{15}$ $cm^{-3}$ even though the ionization degree is rather small. As for the electron temperature $T_e$, it shows non-equilibrium natures inherently due to the short residence time in small space or short duration of pulsed discharge in the generation. Taking the advantage of these non-equilibrium properties, microplasmas have been applied to various purposes such as material syntheses, surface treatments, environmental and biomedical issues, etc. In this talk, I would like to introduce some examples of new schemes of microplasma sources with their characterizations by various diagnostic methods; we have been applying optical emission spectroscopy (OES), laser absorption spectroscopy (LAS), and laser-induced fluorescence spectroscopy (LIF) for the measurements of excited and ionized species as well as THz time-domain spectroscopy (TDS) and infrared $CO_2$ laser heterodyne interferemetry for plasma parameters. In addition to the microplasma generation in usual gas phase, we have been trying to use atmospheric gases with liquid vapors (mists) and aqueous solutions with micro bubbles as artificial media of microplasmas under controlled (characterized) conditions. As one of the examples, by using a fabric electrode assembly weaved with insulated wires, we have succeeded in the generation of microplasmas in $H_2$ or $O_2$ bubbles produced underwater by electrolysis. Those results will be explained together with some examples of their potential applications.

9:20am **PS1-ThM5 Atmospheric Dielectric Barrier Glow Discharges at High Overvoltage**, ***B.D. Schultz***, *A.R. Martin, M.A. Ray, G.E. McGuire, W.M. Hooke*, International Technology Center

Atmospheric dielectric barrier plasma glow discharges in pure nitrogen gas have been generated under overvoltage conditions produced with a custom high voltage source. A voltage rise time of 25 ns at 20-30kV is readily achieved by the source and is sufficient to create overvoltage conditions in excess of three times the DC breakdown voltage of nitrogen. These large overvoltage conditions occur because the rise-times required to achieve peak voltage are shorter than the lag time between the pulse crossing the threshold voltage and the onset of a discharge. Overvoltage conditions prior to discharge have been predicted to produce significantly higher average electron energies in the discharge and to produce high instantaneous power densities. Experimentally current densities have been achieved well in excess of 10 $A/cm^2$ for homogeneous glow discharges of pure nitrogen gas at atmospheric pressure with total pulse currents of 1 kiloamp having been obtained. The overvoltage potential on the electrodes enables manipulation of the reduced electric field, but additional control can also be garnered through increases in the gas temperature and/or decreases in the chamber pressure along with the applied overvoltage. This paper will emphasize the correlation between the overvoltage conditions, the dielectric material properties, temperature, and small deviations in pressure to the electrical charge transfer, optical properties, and propagation mechanisms of the glow discharge. This work was supported in part by ARL and AFRL.

9:40am **PS1-ThM6 Decoloration of Organic Dyes by Bipolar Pulsed Electrical Discharge in Aqueous Solution**, ***Š. Potocký***, *N. Saito, O. Takai*, Nagoya University, Japan

During recent years plasma systems in liquid have become a topical interest. They open new possibilities in wastewater treatment. Those systems are able to produce highly active species which finally results in conversion of the organic to innocuous materials. Nevertheless, the drawback of such system meets with the requirement of very high voltage for sustaining the plasma discharge and relatively low energy efficiency. Another important process is the erosion of the electrodes that limits the operating lifetime or leads to the pollution of treated water with metal particles released from the electrodes. We demonstrate operation of solution plasma process under relatively low discharge voltage (below 4 kV) and two different plasma regimes with pulse energies in mJ range using a high frequency bipolar pulsed DC power supply. It can be operated up to the repetition frequency of 30 kHz with a pulse width range from 2 μs to 10 μs and a maximum voltage and current of ±6 kV and 7 A, respectively. The oxidative decoloration of organic dyes by the bipolar pulsed discharge plasma between needle-to-needle electrodes in water solution has been investigated in two discharge modes: (i) corona, (ii) spark/streamer mode. Ratio between H-alpha and hydroxyl radical emission line intensity differ by two orders of magnitude in those two modes even for high value of solution conductivity (1 mS/cm) which is close to typical value of a wastewater. The current-voltage characteristics of the system together with an optical emission spectroscopy of plasma discharge were used to characterize regimes of plasma discharge operation. Analysis of generated hydrogen peroxide concentration by colorimetric method using titanium reagent and the absorption spectroscopy was performed. Measurement of electrodes erosion and metal concentration (by inductively coupled plasma mass spectroscopy) due to solution plasma process was also carried out indicating obvious difference in two modes of plasma discharge operation.

10:40am **PS1-ThM9 Surface Modification of Ultra High Molecular Weight (UHMW) Polyethylene Films Using Atmospheric Pressure Dielectric Barrier Discharges**, ***D.D. Pappas***, *K.E. Strawhecker, A.A. Bujanda*, United States Army Research Laboratory

In this work, dielectric barrier discharge (DBD) plasmas, operating in nitrogen, air and helium-oxygen at atmospheric pressure, are used to modify the surface properties of ultra high molecular weight polyethylene films. The imposed changes of the hydrophilicity, chemical composition and roughness of the surface appear to have a dependence on the DBD operating parameters such as processing duration and discharge power as well as the nature of the gas being used for the plasma treatment. Contact angle and X-ray photoelectron spectroscopy (XPS) data reveal that in all cases the plasma exposed surfaces exhibit improved wettability that can be attributed to the mild oxidation of polyethylene as confirmed by XPS analysis. Atomic force microscopy (AFM) results show that longer processing duration and higher oxygen concentration are key for increased surface roughness, a factor affecting the adhesion properties of the film. Standard lap-shear evaluations reveal that plasma treatments may lead to significant increases in the bond strength of polymer films and metallic/polymeric substrates and changes in modes (adhesive vs. cohesive) and loci of failure. The plasma treatments increase the mechanical interlocking and frictional energy dissipation effects when bonded to a substrate. Changes in other mechanical properties are also investigated. Most importantly, this uniform modification occurs within a few seconds of exposure, time comparable to continuous on-line industrial processing.

11:00am **PS1-ThM10 The Discharge Characteristics of an Industrial Scale Atmospheric Pressure Uniform Plasma Processing System**, ***W. Graham***, *D. Della Croce, L. Schaper*, Queens University Belfast, Northern Ireland, *L. O'Neill, A.M. Hynes*, Dow Corning Plasma Solutions, Ireland

Time and space-resolved electrical, optical and imaging characterisation of a commercial, 1800cm$^2$ atmospheric pressure plasma system, operating with polymer film is reported. . The system is based on a dielectric barrier discharge operated in air with flowing helium. The system is optimized for plasma treatment, rather than the physical appearance of the plasma. The Dow Corning Plasma Solutions LabLine™ system establishes discharges in two back to back, identical 340mm x 300mm transparent, electrode structures each with an inter-electrode gap of 5mm. The driving power supply produces a sinusoidal voltage, of up to 20 kV peak to peak, at frequencies of around 20 kHz. This is applied to the two internal electrodes. The outer electrodes are grounded. Helium is introduced from the top of the electrodes. Polyethylene Terephthalate (PET) polymer film could be suspended in the centre of the electrode gap, parallel to the glass dielectrics. Standard high voltage and current measurement techniques were used monitor the voltage applied to the electrodes and the current (Id) drawn through the power cable to the electrode assembly. A fast photomultiplier tube was used to measure the temporally resolved emission from the discharge while the spatially and temporally resolved behaviour of the discharge was studied by imaging the electrodes and the electrode gap onto a gated ICCD. The imaging indicates that with or without polymer film present, static or moving, radially uniform discharges, persisting for a few microseconds, are consistently created at the same phases of the applied voltage. The number of discharges increases with increasing input power and hence applied voltage. The structure of the discharge emission is suggestive of that of an atmospheric pressure being most intense at the cathode and showing evidence of a dark space and much less intense emission beyond that. At higher input powers, when the applied voltage considerably exceeds the initial breakdown voltage, these discharges occur so frequently that they sustain and enhance these structured discharges for periods of up to 25 µs. In the presence of the polymer film the discharge was generally more intense in the region occupied by the film and always produced emission between the polymer and the cathode. The authors wish to thank Dr. D. Dowling and B. Twomey of U.C. D. for their support and assistance and gratefully acknowledge EPSRC and Dow Corning support for of D. D. C.

11:20am **PS1-ThM11 Influence of Air and Water Vapour Contaminations on the Atmospheric Pressure PECVD of Fluorocarbon Thin Films**, ***F. Fanelli***, Univeristy of Bari, Italy, *R. d'Agostino, F. Fracassi*, University of Bari, Italy

Low pressure plasma-enhanced chemical vapour deposition (PECVD) of fluorocarbon films has been extensively studied in the last decades. Very recently atmospheric pressure dielectric barrier discharges (DBDs) have been addressed as an attractive route towards the deposition of fluoropolymers, nevertheless, the utilization of this approach is still a challenge. Research efforts should be devoted to evaluate if DBDs can actually be advantageous compared to low pressure plasmas; for this purpose, besides the fundamental investigation of fluorocarbons fed DBDs, it is also important to gain insights into the influence of contaminants such as air and water vapour. The presence of these contaminants into the atmospheric pressure reactor could have, in fact, serious detrimental effects on the overall deposition process because it might result in a drastic decrease of the F/C ratio of the films, in the uptake of oxygen and nitrogen as well as in deposition rate reduction. On the other hand, the knowledge of the highest level of contamination compatible with an acceptable process performance and consequently the possibility of depositing fluoropolymers in “contaminated” environments could allow to reduce the cost of plasma processes and reactors. For these reasons we decided to evaluate the influence of air and water vapour contaminations on the PECVD of fluoropolymers in atmospheric pressure cold plasmas. Controlled amounts of air and water vapour have been added to a DBD fed with argon-hexafluoropropene (Ar-$C_3F_6$). The discharge regime has been clarified by electrical measurements, while film characteristics have been studied by FTIR, XPS, WCA measurements and SEM. Gas phase has been investigated by optical emission spectroscopy and the stable species contained in the gas effluent have been analyzed using gas chromatography coupled with mass spectrometry, in order to have indications on the reactive fragments generated inside the discharge. The results obtained in this work show that Ar-$C_3F_6$ DBDs allow to deposit coatings with a deposition rate of 56 nm/min and a XPS F/C ratio of 1.7. Contaminants addition causes a slight variation of the F/C ratio and a decrease of the deposition rate. In particular, if the [Air]/[$C_3F_6$] and [$H_2O$]/[$C_3F_6$] ratios in the feed are kept below 0.25 and 0.125, respectively, the variation of the F/C ratio is negligible and the deposition rate remains higher than 45 nm/min.

## Plasma Science and Technology
## Room: 306 - Session PS2-ThM

## Plasma Modeling
**Moderator:** D.J. Economou, University of Houston

8:00am **PS2-ThM1 Wave and Electrostatic Coupling in Dual Frequency Frequency Capacitively Coupled Plasmas Utilizing a Full Maxwell Solver***, ***Y. Yang***, *M.J. Kushner*, Iowa State University

Dual frequency, capacitively coupled plasma (DF-CCP) tools are being developed for etching in microelectronics fabrication with the goal of separately controlling the production of etch precursors and ion energy delivered to the wafer. These tools typically use a high frequency (10s to 100s MHz) to sustain the plasma and a low frequency (a few to 10 MHz) for ion acceleration. With an increase in both the high frequency and wafer size, electromagnetic wave effects (i.e., propagation, constructive and destructive interference) can affect the spatial distribution of power deposition and reactive fluxes to the wafer. These effects are difficult to computationally address due to the coupling between electromagnetic and electrostatic fields, the latter of which is responsible for the formation of the sheath. In this talk, we discuss results from a computational investigation of high frequency effects in DF-CCPs. A 2-dimensional Maxwell equation solver utilizing Finite Difference-Time Domain techniques capable of resolving wave and electrostatic effects in arbitrary geometries was developed and incorporated into the Hybrid Plasma Equipment Model. To capture the high frequency heating, excitation rates are provided by spatially dependent electron energy distributions generated by a Monte Carlo simulation. The method of solution will be discussed and validation will be made by comparison with experiments for single frequency excitation. Experimental trends of the transitioning of the plasma density from flat to edge to center peaked (corresponding to electrostatic, skin depth and wave dominated regimes) with increasing frequency are captured by the model. Results from a parametric investigation of DF-CCPs (LF ≤ 10 MHz, HF ≥ 50 MHz) in polymerizing gas mixtures will also be discussed. Assessments will be made of the changes in power deposition and electron impact ionization profiles as a function of frequency, the location of power coupling and intervening materials.

*Work supported by the Semiconductor Research Corp., Tokyo Electron Ltd. and Applied Materials Inc.

8:20am **PS2-ThM2 Three-Dimensional Modeling of Capacitively-Coupled Plasmas with Asymmetric Reactor Elements**, ***J.A. Kenney***, *S. Rauf, K. Collins*, Applied Materials, Inc.

Much of the focus in past plasma uniformity studies has been on center-to-edge non-uniformity, which can generally be addressed through careful plasma reactor design and process optimization. As plasma processing uniformity requirements grow more stringent, there is an increasing emphasis on the characterization of asymmetric reactor elements which may give rise to azimuthal non-uniformities. The complexity of these systems can make experimental analysis of isolated components difficult, however, which has provided an impetus for the development of a three-dimensional fluid plasma model. Herein, we describe the model and its use in the investigation of several azimuthally asymmetric elements in typical plasma processing reactors. In our three-dimensional model, charged species densities are computed by solving continuity equations for all species using the drift-diffusion approximation. The coupled set of charged species continuity equations and Poisson equation, which governs the electrostatic fields, is solved implicitly in time. The electron temperature is determined by solving the electron energy equation. The model also includes the full set of Maxwell equations in their potential formulation, Kirchhoff equations for the external circuit, and continuity equations for neutral species, along with non-uniform mesh generation to better resolve regions of interest. Using this model, we have investigated several azimuthally asymmetric components with the potential to perturb the plasma density, ion flux at the wafer, and electric fields. Ar is the feed gas in all simulations. For 13.56 MHz capacitively coupled plasma (CCP) discharges with peak plasma densities near the electrode edges, asymmetric elements include discontinuities of various sizes and locations in the reactor wall (e.g., diagnostic ports, slit valve) as well as the presence of off-axis circular plates surrounding the lower electrode. For 162 MHz CCP discharges with densities typically peaking in the reactor center, the impact of electrode planes aligned off-normal to each other is investigated, for several degrees of tilting and at different electrode gaps. Fourier analysis is used as appropriate to quantify the degree of perturbation induced by each asymmetric component.

### 8:40am **PS2-ThM3 Flow-Plasma Interactions in Plasma Etching: A 3-Dimensional Computational Investigation**, ***A. Balakrishna***, *S. Rauf, K. Collins*, Applied Materials, Inc.

Plasma etching is a complicated process where plasma dynamics, gas and surface chemistry, and fluid flow all have significant influence on the processing results. Flow effects in commercial plasma etching reactors cannot be accurately captured in 2D models or 3D plasma-only models. While 3D flow-only models have been used to evaluate the redistribution of important plasma species and to suggest hardware improvements, this approach limits the understanding of the influence of fluid flow on the plasma. In particular, hardware changes made to improve flow symmetry impact plasma distribution, and vice versa. We have developed an integrated 3D flow and plasma model to enable this concurrent optimization. In this model, the Navier-Stokes equations in cylindrical coordinates were solved using a finite volume method. The equations were discretized using flux balances on each computational cell. The pressure distribution was computed using the SIMPLE method,[2] which corrects the flow and pressure fields to fulfill mass conservation. The calculated flow distribution was passed to the plasma model, which includes the full set of Maxwell equations in their potential formulation. The vector potential is solved in the frequency domain after each cycle, with current sources computed using results from the previous cycle. The coupled set of equations governing the scalar potential and drift-diffusion equations for all charged species are solved implicitly in time. The model also includes the electron energy equation, Kirchhoff equations for the external circuit, and continuity equations for neutral species. The 3D fluid-plasma model was used to understand the operation of capacitively coupled plasmas operating at 13.56 and 160 MHz in this paper. Both electropositive (Ar) and electronegative (O2) gases were considered. Comparison of the solutions with and without fluid flow interaction allowed us to separate the effects of flow and plasma on species distribution in the chamber. At sufficiently high flow rates, azimuthal flow non-uniformities were reflected in the plasma species distributions.

[1] J. Kenney, S. Rauf and K. Collins, AVS 2008.

[2] S.V. Patankar and D.B. Spalding, Int. J. Heat Mass Transfer, vol. 15, pp. 551-559 (1972).

### 9:00am **PS2-ThM4 Modeling of Micro-Scale Si Etching under Plasma Molding in 2f-CCP in $SF_6/O_2$**, ***F. Hamaoka***, *T. Yagisawa, T. Makabe*, Keio University, Japan

Reactive ion etching (RIE) used for fabricating a nanometer-scale element of the semiconductor device has been applied to the process of a micro-scale etching in micro-electro-mechanical system (MEMS). Plasma molding is one of the important issues in micro-scale etching with several tens or hundreds of micrometers in width and depth.[1] In our previous study, the influence of the ion transport under the distorted sheath potential, i.e., plasma molding, on the anisotropic Si etching was numerically investigated without considering the neutral reaction.[2] In addition to the effect of ions, we developed the gas-phase and surface model for Deep-RIE of Si in a 2f-CCP in $SF_6/O_2$ under competition between Si etching and passivation layer formation, including the effect of plasma molding.[3] These investigations imply that the ions incident on the wafer under the distorted sheath potential by plasma molding remove the passivation ($SiO_xF_y$) layer on the sidewall and bottom corner, suppressing etch anisotropy. In this study, we numerically investigate the feature profile evolution of Deep Si etching under the presence of the plasma molding in 2f-CCP in $SF_6/O_2$ as functions of gas mixture and pressure with different widths of micro-scale pattern. The sidewall etching is suppressed drastically with increasing the oxygen mixture ratio due to forming the passivation layer by oxygen radicals on the Si surface. In $SF_6/O_2$(50%) at 300 mTorr, the etching profile of 250μm-wide-pattern is distorted especially at the bottom corner because of the excess ions with radially distorted angular distribution by plasma molding. On the other hand, at 100 mTorr, the etching profile at the bottom is flattened by chemical effect at the center due to the smaller flux of $O(^3P)$ than that at 300 mTorr; however, the sidewall etching occurs slightly. We will also discuss the etching profile with different pattern widths under plasma molding in 2f-CCP in $SF_6/O_2$.

[1] D. Kim and D. J. Economou, IEEE. Trans. Plasma Sci., vol. 30, no. 5, pp. 2048–2058, 2002.

[2] F. Hamaoka, T. Yagisawa, and T. Makabe, Jpn. J. Appl. Phys., vol. 46, no. 5A, pp. 3059-3065, 2007.

[3] F. Hamaoka, T. Yagisawa, and T. Makabe, IEEE Trans. Plasma Sci., vol. 35, no. 5, pp. 1350-1358, 2007.

### 9:20am **PS2-ThM5 Computer Simulations of Processing Plasmas**, ***A. Bogaerts***, University of Antwerp, Belgium **INVITED**

In this talk, an overview will be given of different modeling activities going on in our research group, for the aim of improving the applications of processing plasmas. There exist several approaches in literature to model gas discharge plasmas, each with their own advantages and disadvantages. In this presentation, several examples will be given of plasma modeling activities going on in our research group, to illustrate the capabilities and limitations of the various modeling approaches. More specifically, the following topics will be presented: Fluid modeling for describing the detailed plasma chemistry, leading to nanoparticle formation in dusty silane and acetylene discharges; Fluid modeling for describing dielectric barrier discharges (DBDs), used e.g., for surface treatment, but also for biomedical or environmental applications; PIC-MC modeling for describing magnetron discharges, for sputter-deposition applications of thin films; Hybrid MC-fluid modeling for describing inductively coupled plasmas (used for etching applications in the microelectronics industry) and glow discharges (used for analytical spectrochemistry applications). In each case, both the model and the type of discharge will be briefly outlined, and typical calculation results will be presented. Furthermore, it will be demonstrated why this particular modeling approach is most suitable for this application. Beside these computer models for the plasma itself, it is also of great interest to simulate the interaction between the plasma and the walls of the plasma reactor, because (i) this defines the boundary conditions of the plasma simulations, and (ii) it is essential for important applications such as thin film deposition and surface etching. For this purpose, we apply molecular dynamics (MD) simulations. The capabilities and limitations of MD simulations will be illustrated for the case of plasma deposition of nanostructured carbon materials (nanocrystalline diamond thin films or carbon nanotubes).

### 10:40am **PS2-ThM9 Simulation of Profile Evolution in Shallow Trench Formation by Plasma Etching**, ***J. Hoang****, *J.P. Chang*, University of California, Los Angeles

In this work, a Monte Carlo based feature scale model was developed to accurately portray the profile evolution during shallow trench isolation etch (STIE) in chlorine based plasmas. A novel surface representation eliminates the artificial surface flux fluctuations due to the highly sloped sidewall features under simulation and the discrete cell nature of the simulation domain. It also enables a precise calculation of the surface normal, which dictates the trajectory of the reflected reactive species that control the profile evolution. The number of particles simulated is estimated from the depth and width of the etched profiles determined by scanning electron microscopy (SEM), with the assumption that the etch processes occur at high neutral-to-ion flux ratios. Through a set of carefully planned design of experiments (DOE) in which the effects of plasma density and plasma chemistry were assessed, the model was shown to accurately predict key features of STIE profiles, including microtrenching, mask faceting, and sidewall tapering, as a result of changing neutral-to-ion ratio, the mean ion energy, ion energy and/or angle distribution function. A two-dimensional numerical fluid model was developed to investigate the dual-coil and dual-feed reactor design on the radial profiles of plasma species, namely etch products and positive ions. The dual-coil parameter was determined to be effective in tailoring the radial ion flux profile at pressures higher than 20 mT, while the dual-feed parameter was shown to alter the etch product transport in the convection-dominant flow regime. Coupling of the reactor scale model to the feature scale model allowed investigation of subtle yet important changes in the etched feature profile from the center to the edge

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* PSTD Coburn-Winters Student Award Finalist

of the wafer. This hybrid model suggests that the radial decrease in the etch depth from wafer center to edge, seen from a set of DOE, is caused by an inherent net neutral-to-ion ratio decrease. In addition, the increase in the silicon sidewall angle from wafer center to edge can be qualitatively explained by a decrease in the concentration of the etch products. To study the local variations at the die/meso scale, the simulation domain is expanded to study the effects of etch product distributions at the die level.

11:00am **PS2-ThM10 Investigation of Micro-Trenching, Bowing and Charge Accumulation on Mask using a Dry Etching Simulator Designed for Low-Pressure High-Density Plasma**, ***J. Saussac**, J. Margot,* Université de Montréal, Canada, *M. Chaker*, INRS-Energie, Matériaux et Télécommunications, Canada

The development of new sub-micron technologies requires a fundamental understanding of device fabrication processes in order to be able to push the technology to its limits. In particular, in the context of plasma etching, the quality of patterning critically depends upon a number of plasma characteristics and on the surface reactivity with respect to the plasma species. Numerical simulation is of great interest for providing insights into the physics underlying various processes and to indentify the etching control mechanism. We developed a cellular Monte-Carlo-based dry etching simulator designed for low-pressure high-density plasma. The simulation code has been validated for various experimental profiles, namely Si, $SiO_2$, $SrTiO_3$ and Pt thin films etched in Ar and Ar/$Cl_2$ plasmas. The observations of both micro-trenching, due to ion scattering on sidewalls, and bowing, due to lateral etching, are well reproduced for various profile widths from 4 µm to 500 nm, which validates the simulation approach. We also investigated the effect of electrical mask charging during Pt etching in Ar plasma. Assuming an electrical field near the mask surface through positive charge accumulation yields the angular deviation of impacting ions. It will be shown that the etching profile obtained by our simulation is in good agreement with that observed from scanning electron microscopy.

11:20am **PS2-ThM11 Atomic-Scale Numerical Simulations of Surface Reactions in Carbon-Based Thin Film Deposition Processes**, ***Y. Murakami**, S. Horiguchi,* CANON ANELVA CORPORATION Japan, *S. Hamaguchi*, Osaka University, Japan

Diamond-like carbon (DLC) films have attracted much attention in the coating technology community. In our experiments, DLC films as protection layers for data recoding disks have been developed. Characteristics of DLC films are generally determined by the amount of $sp^3$ hybridized bonds present in the films, which may be controlled by hydrocarbon species and its injection energy used for the deposition process. Various mechanisms of formation of $sp^3$ hybridized bonds in DLC films have been proposed,[1] but some details are yet to be understood better. In this work, in an attempt to establish a high quality DLC deposition process, we have used molecular dynamics (MD) simulations to understand interaction between carbon containing gaseous radical species and an amorphous carbon (α-C) surface. Especially focused in this work are interactions of incoming $CH_3$ and CH species with an unhydrogenated α-C surface. The interatomic potential functions used in this study are the same as those used in Ref.2. In simulations charge-neutral $CH_3$ or CH radical species are injected 300 times ($7.5\times10^{15}cm^{-2}$ dose) normally into the top surface of the substrate with incident energies in the range from 2eV to 50eV. The substrate temperature is kept at room temperature (300K) at the beginning of every injection. In our results, it is found that the sticking probabilities of both C and H atoms of the incoming to the substrate surface depend on the incident energy. It is also shown that the sticking probability of a CH radical is higher than that of a $CH_3$ radical in the entire energy range. It is due to the fact that a CH radical has more dangling bonds that energetically favor forming complete bonds with C atoms of the substrate. The fraction of $sp^3$ hybridization bonds is also found to be higher in the case of $CH_3$ injections. This indicates that, with the availability of more hydrogen atoms, a carbon atom tends to form more diamond-like structures. These results may be used for the development of deposition processes for high quality DLC films.

[1] J. Robertson, Materials Science and Engineering, R37 (2002) 129.

[2] H. Yamada and S. Hamaguchi, Plasma Phys. Control. Fusion 47 (2005) A11.

11:40am **PS2-ThM12 Coupling Reaction Kinetics of Gas Phase, Reactor Wall, and Wafer Surface in $C_4F_8$ and $SF_6$ Plasmas with Global Models**, ***G. Kokkoris**, E. Gogolides,* NCSR Demokritos, Institute of Microelectronics, Greece, *A. Goodyear, M. Cooke*, Oxford Instruments Plasma Technology, UK

$C_4F_8$ plasma has been used for dielectric etching in microelectronics and, in combination with $SF_6$ plasma, for deep Si etching during the Bosch process in the area of micro-electro-mechanical systems fabrication. $C_4F_8$ is also met in plasma enhanced chemical vapor deposition of fluorocarbon (fc) films. Several models for $C_4F_8$ plasmas have been reported,[1] while there is a lack of models for $SF_6$ plasmas[2] in low pressure conditions. None of the models has focused on the interaction of the bulk phase with the reactor surfaces. The importance of the interaction increases as the constraints for manufacturing become stricter; it can affect the reproducibility of the process.[3] In this work, a 0D or global type model for $C_4F_8$ and $SF_6$ plasmas is formulated and is combined with a surface reaction model. The combined model, not only takes into account the effect of the surface reactions on the species densities in the bulk, but also allows the calculation of derived outputs which extend the potential experimental measurements for the validation of global models. In particular, it allows the calculation of a) the pressure change after the ignition of the discharge which links to the degree of dissociation of the parent gas, b) the effective sticking coefficients of the species which signify the net consumption of the species on the reactor surfaces and are the values measured in the experiments, and c) the deposition rate and the ratio of F/C of the fc film ($C_4F_8$ case), which can affect e.g. the $SiO_2$ etching selectivity over Si and the dielectric constant of the film. The results of the combined model compare well with measurements of pressure change and densities of F atoms, $CF_x$ radicals, and ion flux versus power and pressure in an inductively coupled plasma reactor. For $C_4F_8$, the parent gas is vastly dissociated, $CF_4$ dominates after 1000 W, and production of $CF_3$ at the reactor walls is predicted. For $SF_6$, the loading phenomenon during Si etching is predicted.

[1] G. I. Font, W. L. Morgan, and G. Mennenga, J. Appl. Phys. 91, 3530-3538 (2002).

[2] C. Riccardi, R. Barni, F. De Colle, and M. Fontanesi, IEEE Trans. Plasma Sci. 28, 278-287 (2000).

[3] G. Cunge, B. Pelissier, O. Joubert, R. Ramos, and C. Maurice, Plasma Sources Sci. Technol. 14, 599-609 (2005).

## Advanced Surface Engineering
## Room: 204 - Session SE+TF+NC-ThM

## Glancing Angle Deposition (GLAD) I
## Moderator: T. Karabacak, University of Arkansas at Little Rock

8:00am **SE+TF+NC-ThM1 Sculptured Thin Films: Something Old, Something New, Something Borrowed, Something Blue**, ***A. Lakhtakia***, Pennsylvania State University **INVITED**

Sculptured thin films (STFs) are assemblies of parallel shaped columns with nanoscale features.[1] The demonstrated optical and biological functionalities of STFs suggest their classification as nanoengineered metamaterials. Deliberate engineering of the shape of columns was accomplished about 35 years before the formal conceptualization of STFs as optical materials in the early 1990s. Thereafter, the language of liquid crystals was borrowed to describe their optical constitutive properties. The design of columnar morphology for STF-based devices to engineer the optical polarization state became well-established about five years ago. The research front for optical applications of STFs now comprises electrically controllable optical filters, light sources of specific polarization states, and plasmonics. High-quality optical performance may necessitate post-deposition processes that result in blue-shifting of spectral features. In contrast, high precision in morphology appears unnecessary for using STFs as platforms for cell cultures.

[1] A. Lakhtakia and R. Messier, Sculptured Thin Films (SPIE Press, 2005).

8:40am **SE+TF+NC-ThM3 Randomness and Roughening in Glancing Angle Deposition**, ***K. Robbie**, T. Brown,* Queen's University, Canada, *S. Asgharizadeh, M. Sutton*, McGill University, Canada

The unique highly-porous nanostructures created with Glancing Angle Deposition are a direct result of the randomness inherent to the condensation of atomic or molecular vapors. This randomness arises through quantum indeterminism in the atom-by-atom evaporation of the source material. At one extreme of film growth conditions, when adatom diffusion is high, the influence of vapor-substrate geometry is minimized and the resulting films are typically dense with isotropic structure and properties - in essence this is the regime of molecular beam epitaxy. When adatom mobility is reduced (e.g. through reduced temperature or the introduction of a reactive gas) geometrical effects become increasingly important and a balance develops between roughening due to the random arrival of atoms and smoothing due to the reduced, but still finite, adatom diffusion. Films grown under these conditions with normal-incidence vapor can be quite dense, yet the film surface will always roughen due to the random arrival of the vapor atoms, eventually resulting in a cauliflower-like fractal morphology. The unique nanostructures of GLAD are created when geometrical shadowing is used to amplify randomness-induced roughening - requiring the vapor to arrive at an angle larger than approximately 70 degrees from the substrate normal. We present here the first experimental observation, through x-ray reflectivity (XRR) measurements of thin silicon films, of the transition to the glancing angle growth regime. We find that film porosity increases as a function of thickness in the GLAD regime, whereas it decreases with thickness under the same growth conditions yet with nearer-normal vapor incidence. Silicon films deposited at room temperature onto rapidly rotating substrates exhibit linearly increasing density as a function of thickness when deposited at vapor incidence angles of less than 70 degrees, and linearly decreasing density (increasing porosity) when deposited at incidence angles above 70 degrees. We also show that significant 'filling-in' can occur during glancing-angle growth, where vapor deposits some distance below the growing film surface. These XRR measurements provide valuable new insight into the glancing angle deposition growth process, and will help to refine film nanostructure simulation and design models.

9:00am **SE+TF+NC-ThM4 Scaling of Nanorods during Glancing Angle Deposition: Effect of Surface Diffusion**, ***S. Mukherjee***, *D. Gall*, Rensselaer Polytechnic Institute

Ta, Al, and Cr nanorods, 65–430 nm wide and 440 nm tall, were grown by glancing angle sputter deposition onto continuously rotated Si(001) substrates from a deposition angle of 84º at substrate temperatures $T_s$ = 300–1125 K. Surface diffusion is negligible at low homologous temperatures $T_s/T_m < 0.08$ ($T_m$: melting point) and for systems with a high activation energy for surface diffusion $E_m$. This leads to a chaotic growth process where the surface morphological evolution is controlled by long-range shadowing interactions and the rod width w (= 58 nm) at a constant height h (= 400 nm) is material independent. However, at higher growth temperatures, w increases with $T_s$ and scales with $T_s/T_m$ for all investigated metals as well as for data from the literature. This is attributed to an increase in the average island size on the growth surface which results in additional shadowing interactions and a chaotic divergence in the microstructure. Applying mean-field nucleation theory and non-linear dynamics within the kinetically limited growth regime yields a Lyapunov exponent $\lambda$ of 0.033 for the divergence from the zero-temperature morphology and an effective $E_m$ that scales with the melting point according to $E_m = 2.46kT_m$. The data also suggests a transition from a 2D to a 3D island growth mechanism as $T_s$ increases from below to above a critical temperature $T_c = 0.24T_m$. The growth exponent p decreases monotonously from 0.5 to 0.31 as $T_s$ increases from 300 K to $T_c$, in agreement with Meakin and Krug's model and Mullins-Herring model for 2+1 dimensional moving interfaces. However, p exhibits a discontinuity at Tc and becomes anomalous (p > 0.5) for $T_s > T_c$.

9:20am **SE+TF+NC-ThM5 Glancing Angle Deposition on Rotating Patterned Substrates: Experiment and Simulation**, ***C. Patzig***, Leibniz-Institute of Surface Modification Leipzig, Germany, *T. Karabacak,* University of Arkansas at Little Rock, *B. Fuhrmann,* Martin-Luther-University Halle, Germany, *B. Rauschenbach*, Leibniz-Institute of Surface Modification Leipzig, Germany

When glancing angle deposition is combined with a continuous substrate rotation, the growth of nanostructures with various shapes such as vertical posts, spirals and screws is possible. The shape is controllable with the ratio $\rho = r/\omega$ of the deposition rate r to the rotational speed $\omega$. Besides the control of $\rho$, other deposition parameters such as the deposition angle $\beta$ between particle flux and substrate normal, or the substrate temperature can be used to alter morphology and density of the grown sculptured thin films. Additionally, the use of a patterned substrate as an array of artificial seeds for the incoming deposition flux can lead to the growth of periodically arranged nanostructures. Here, nano sphere lithography was used to structure Si(100) substrates with Au dots in both hexagonally close packed and honeycomb arrangement as templates for the subsequent glancing angle deposition that was done by ion beam sputter deposition of a Si target. The influence of $\rho$, $\beta$, and the height of the Au seeds h on the morphology of the Si nanostructures for the case of the honeycomb pattern is discussed and compared with Monte Carlo simulations of glancing angle deposited sculptured thin films on templated substrates. It is found that in both experiment and simulation, depending on $\rho$ either periodically arranged spiral-like or vertical column-like structures are grown, whereas changing $\beta$ from 0° to a glancing 85° shifts the film morphology from dense with honeycomb-like arranged caps over partially grown together nanocolumns with hexagonally arranged pores in-between to separated nanostructures that replicate the templates honeycomb arrangement. Additionally, it was found both experimentally and in simulations that glancing angle sputter deposition on rapidly rotating substrates causes nanocolumns with triangular cross section on honeycomb templates and with circular cross sections on hexagonally close packed templates, showing that not only the inter-seed-distances, but also the symmetry of the template pattern influences the form of the growing nanostructures.

10:40am **SE+TF+NC-ThM9 Growth of Al Nanowhiskers on the Patterned Substrate by Glancing Angle Deposition at High Temperature**, ***M. Suzuki***, *R. Kita, K. Hamachi, K. Nakajima, K. Kimura*, Kyoto University, Japan

Recently, we have found that peculiar metal (Al, Fe, Ag, Au etc.) nanowhiskers grow when metal is deposited at a glancing angle on a high-temperature substrate (HT-GLAD). The key factors for producing nanowhiskers are a glancing deposition angle larger than 80° and a temperature higher than almost half of the melting point of the metal. Since the growth of the nanowhiskers may be concerned with the general crystal growth mechanisms, an understanding of the growth mechanisms will provide a novel technique to fabricate nanostructures. Further, if the growth of nanowhiskers is controlled, metal nanowhiskers will become important components for nanoelectromechanical devices because of their mechanical compliance, high electric and thermal conductance, catalysis, plasmonic properties, magnetism, etc. In order to understand the effect of the detailed geometric deposition condition on the growth of nanowiskers, we have demonstrated HT-GLAD of Al on a heated substrate with trench patterns. Al was deposited on a surface-oxidized Si(110) substrate using an electron beam (EB) evaporation apparatus specially designed for HT-GLAD. Six groups of trenches with a nominal width of 1, 3, 5, 10, 15, and 20 µm, respectively, and a depth of 1.7 µm were prepatterned along the direction. The substrate temperature during the deposition was maintained constant at a temperature of 390 °C. By choosing an appropriate substrate attitude during the deposition, the deposition angle on the sidewalls of the trenches was kept constant at 85°, while that on the surface was varied between 55° and 87°. The amount of Al deposited on the sidewalls was 30 nm in average thickness for all samples. The number of nanowhiskers growing on the sidewalls significantly increased with deposition angle on the surface. This suggests that Al atoms deposited in front of the growing nanowhiskers play an important role in the growth of nanowhiskers. The directive migration and/or reflective scattering are possible candidates for the transport process of the deposited atoms.

11:00am **SE+TF+NC-ThM10 Characteristic Length Scale of Nanorods**, ***H. Huang***, RPI

Glancing angle deposition has led to numerous exotic structures of nanorods. It is natural to ask: what makes nanorods nano. Following the discovery of three-dimensional Ehrlich-Schwoebel barrier, we have discovered a new length scale that dictates the formation of crystalline nanorods. This presentation starts with the physics origin of such length scale, and continues with atomistic simulations demonstrating the variation of the length scale and validation experiments, and ends with design of nanosynthesis based on the knowledge of this new length scale & its experimental validation. It is interesting to note that this length scale is the very reason that nanorods synthesis is possible, even though nanorods had been realized long time ago (and it was patented a decade ago).

11:20am **SE+TF+NC-ThM11 Crystalline Organic Nanocolumn Arrays**, ***J. Zhang***, *I. Salzmann, P. Schaefer, J.P. Rabe, N. Koch*, Humboldt University Berlin, Germany

Nanocolumn arrays based on organic semiconductor materials have significant potential for realizing various devices, such as sensors, field emitters, and nanoelectronic devices, on large-area flexible substrates at room temperature. In our work, crystalline nanocolumnar arrays of two widely studied organic semiconductors, i.e., Fullerene ($C_{60}$) and pentacene were fabricated by glancing angle deposition (GLAD), and characterized by scanning electron microscopy and X-ray diffraction. For both materials, column diameters of typically 100 nm are found on the transparent conductive oxide ITO at the rotation speed of 3 rpm (rounds per minute), essentially independent of column height (up to 360 nm for pentacene). However, on Si-oxide only $C_{60}$ formed nanocolumns, while pentacene exhibited a morphology resembling that obtained by regular normal incidence deposition. The difference is attributed to the different molecular surface diffusion lengths on the substrate. Furthermore, the morphology of nanocolumns on ITO grown by GLAD is studied for molecular materials forming amorphous and crystalline solids. Amorphous tris(8-hydroxyquinoline)aluminum nanocolumn arrays were obtained at sample rotation speeds varying from 0.3 rpm to 30 rpm. For crystalline pentacene, a nanocolumn array formed at a rotation speed of 3 rpm, while a wide distribution of column heights and shapes was formed at rotation speeds of 0.3 rpm and 30 rpm. The incoming molecular flux and molecular diffusion length on column surface, both determined by rotation speed, were found to govern the resulting morphology of crystalline pentacene nanocolumns on ITO.

11:40am **SE+TF+NC-ThM12 Competitive Growth Mechanisms of Aluminum Nitride Thin Films Deposited by Off-Normal Reactive Magnetron Sputtering**, ***D. Deniz,*** University of New Hampshire, *T. Karabacak,* University of Arkansas at Little Rock, *J.M.E. Harper*, University of New Hampshire

We have recently shown that AlN (0002) (c-axis) is tilted abruptly towards the deposition direction as N2 concentration is increased in N2/Ar sputtering gas mixtures. Here we present a Monte Carlo simulation model to describe the phenomenon of sudden c-axis AlN tilt. The model is based on the assumption that AlN islands with their c-axis parallel to substrate normal and AlN islands with tilted c-axis coexist at the initial stages of the growth and they can provide the adatoms with different surface mobilities. It is believed that the adatom mobilities are quenched when N2 concentration reaches a certain amount in the reactive sputtering of AlN. Our model further assumes that adatom mobility differences on different islands result in a growth rate difference of the islands. At the initial stages of the growth, AlN islands with tilted c-axis grow taller due to the lower adatom mobility on these islands. As they grow taller they win the competition and stop the further growth of AlN islands with their c-axis parallel to substrate normal due to shadowing effect. Monte Carlo simulations revealed that the shadowing effect combined with different adatom mobilities promotes the sudden c-axis tilt in AlN thin films.

## 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 Cl$_2$-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 Cl$_2$-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 Assister 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+ ions 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/cm$^2$ 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 nanorippels 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 spectra[1] 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.

[1] I. 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. Grossklaus***, *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 AlAs 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 AlAs 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 (MeCpPtMe$_3$) 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)Me$_3$ 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)Me$_3$ 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-CH$_3$ bond cleavage event. The average cross-section for the electron stimulated decomposition of adsorbed MeCpPt(IV)Me$_3$ via the different pathways at a specific electron beam energy of 500 eV is measured to be 1.5x10$^{-16}$ 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. Yakshinksiy, 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 $(CH_3)_3$-Pt-$C_5H_4CH_3$ (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.

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

[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.

## Surface Science
## Room: 208 - Session SS2+NC-ThM

## Catalysis on Nanoclusters
**Moderator:** J. Hrbek, Brookhaven National Laboratory

8:00am **SS2+NC-ThM1 Hybrid Nano-Oxide System for Oxidation of Methanol at Lower Temperatures**, ***A.S. Karakoti***, *A. Vincent, T. Spalding*, University of Central Florida, *D. Patel*, NJ Institute of Technology, *S. Seal*, University of Central Florida

Paradigm shift in the global energy policy towards cleaner and alternate fuels, arising out of uncontrolled green house emissions and rapid depletion of fossil based fuels, paved the way for various challenging areas of research. Among the various alternatives, direct oxidation of alcohols to hydrogen offer one promising alternative to primary fuels. Hydrogen produced from the alcohols can be used as a primary fuel source for DMFCs. Preliminary work on conversion of methanol to hydrogen and other byproducts, in presence of noble metals such as platinum and gold as catalysts, has shown promising results. However, the use of noble metal catalysts makes the conversion an expensive deal. Nanomaterials such as titanium oxide (titania), zirconium oxide (zirconia), cerium oxide (ceria) have been tried as active catalyst supports in varying range of particle sizes and molar ratios of noble metals with limited success. To overcome the hurdles in the existing systems, we have focused on the hybrid ceria-titania nanostructures synthesized using sol gel and co-precipitation methods for optimizing the efficiency of the catalyst in methanol oxidation. The percent conversion of methanol to various species was studied using an in-house built catalytic reactor coupled to a mass spectrophotometer for analysis of gaseous reaction products. The selectivity and efficiency of the hybrid nano-oxide system as a catalyst support was studied as a function of mixture concentration, percent loading of the noble metal catalyst and the phase structure. Experimental results were normalized with respect to the surface area of the supporting catalysts. The adsorption characteristics of methanol and byproducts on the catalyst surface were evaluated using Diffuse Reflectance Infra-red Fourier Transform Spectroscopy (DRIFTS). Powder samples were characterized using X-ray Diffraction (XRD) and Transmission Electron Microscope (TEM) for determining the phase, particle size and shape of the particles in mixed systems. X-ray Photoelectron spectroscopy (XPS) was used to verify the oxidation state of the metal catalyst as well as mixed ceria-titania supports as a function of molar concentration of the constituents. Preliminary results have shown that the onset temperature for methanol decomposition was as low as $150^{o}$C and both the onset as well as complete conversion temperature varies as a function of molar ratio of ceria to titania.

8:20am **SS2+NC-ThM2 Decomposition of Methanol on High Surface Area Titanium Carbide Films**, ***D.W. Flaherty***, *N.T. Hahn, C.B. Mullins*, University of Texas at Austin

We are investigating the surface chemistry of small alcohols on novel, high surface area, titanium carbide films using a combination of temperature programmed desorption, molecular beam reactive scattering, and infrared absorption spectroscopy. High-surface area catalytically active films can be synthesized by glancing angle deposition of a metal onto a cold surface in a low ambient pressure of gas. The subsequent surface reaction of the two components results in the growth of nano-porous films with controllable stoichiometry and morphology. We have employed this technique, referred to as reactive ballistic deposition (RBD), to deposit nano-structured, high surface area films of metal carbides. It is well known that transition metal carbides have catalytic properties similar in some respects to platinum group metals, with the added benefits of comparatively low cost, high thermal stability, and mechanical durability. Building on our knowledge from the previous investigation of high surface area TiO2 films, we are developing high surface area, porous, transition metal carbide films for the purpose of studying their physical properties and chemical reactivity. Our current work has focused on the deposition and physical characterization of titanium carbide (TiC) films deposited using the RBD technique. Auger electron spectroscopy is used to investigate the stoichiometric dependence of the films on growth conditions. The specific surface area and distribution of binding site energies of the films are measured as functions of growth temperature, deposition angle, and annealing conditions using temperature programmed desorption (TPD) of chlorodifluoro-methane. Results from TPD studies suggest that TiC films grown using the RBD technique have specific surface areas of at least 100 $m^2$/g and are thermally stable to nearly 1000 K. The combination of high surface area and thermal stability suggest that these films could be effectively utilized for heterogeneous catalysis.

8:40am **SS2+NC-ThM3 Catalysis by Atomic-Size Centers**, ***H. Metiu***, University of California, Santa Barbara **INVITED**

We perform density functional calculations to explore the properties of two new classes of catalysts, both consisting of atomic-size active centers. In one class the cation at the surface of an oxide is replaced with another cation which we call a dopant. By an appropriate choice of the dopant-oxide pair we can weaken the bond of the oxygen atoms at the surface of the oxide and make the system a better oxidant and a better oxidation catalyst. Other choices of dopant-oxide pairs will cause the dopant to adsorb oxygen and weaken the O-O bond to activate oxygen for oxidation reactions. A second class of catalysts with atomic-size active center consists of small oxide clusters supported on a different oxide (for example, a $VO_3$ cluster supported on $TiO_2$). Some of the oxygen atoms in the cluster end up bridging two different cations (for example, V-O-Ti) and if the two cations are well chosen, the bridging oxygen becomes active in oxidation reactions. We study the mechanism of methanol oxidation to formaldehyde by $VO_3$ supported on $TiO_2$ and plan to screen a large set of oxide clusters on an oxide for hydrocarbon activation.

9:20am **SS2+NC-ThM5 The Oxidative Dehydrogenation of Methanol by Vanadia Particles Supported on Ceria Thin Films**, ***H.L. Abbott***, *A. Uhl, M. Baron, D.J. Stacchiola, S.K. Shaikhutdinov, H.-J. Freund*, Fritz Haber Institute of the Max Planck Society, Germany

Vanadia particles and monolayer or submonolayer coverage vanadia films supported on metal oxide surfaces have shown high activity for the selective oxidation of alcohols. In particular, methanol oxidative dehydrogenation to formaldehyde occurs readily on ceria-supported vanadia. Although support and coverage effects are known to be important for this reaction, questions remain about the relationship between the structure and the reactivity. Here, a well-defined model system, consisting of vanadia nanoparticles deposited on thin ceria films, has been employed. X-ray photoelectron spectroscopy (XPS), scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRAS), and temperature programmed reaction (TPR) were used to characterize the $VO_x/CeO_2$ model system. XPS measurements indicated that the oxidation state of the vanadium atoms increases with decreasing coverage. Under low coverage conditions, STM images revealed the presence of isolated vanadia species. Vanadyl stretching vibrations detected by IRAS vary between 1000 and 1050 $cm^{-1}$, depending on the coverage and the annealing temperature. Two TPR peaks, corresponding to the selective oxidation of $CH_3OH$ on $VO_x$, were observed, including a new low temperature peak at ~350 K that is believed to correlate with isolated species.

9:40am **SS2+NC-ThM6 Photochemistry of $(NO)_2$ Layers on Alumina-Supported Ag Nanoparticles: Size and Excitation Influences**, *D. Mulugeta, K.H. Kim, K. Watanabe,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany, ***D. Menzel***, Fritz-Haber-Institut der Max-Planck-Gesellschaft and Technical University Muenchen, Germany, *H.-J. Freund*, Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany

The unique electronic and optical properties of metal nanoparticles (MNPs) are caused by their small size compared to typical interaction lengths with photons and electrons, the confinement of excitations in them, and their specific excitations, in particular the Mie plasmon which causes strong field enhancement.[1] Modifications of photochemical reactions occurring on them are expected. We have investigated the photochemical reactions in $(NO)_2$ layers on AgNPs deposited on alumina films, using ns laser pulses off and on the plasmon resonance, and for varied NP size. Photoexcitation of $(NO)_2$ leads to photodesorption of NO as well as photochemical conversion to $N_2O$ and to chemisorbed NO. Results include total removal and conversion efficiencies, desorbed species and their cross sections, and mean translational energies of photodesorbed NO. Excitation in the plasmon resonance strongly enhances yields and cross sections, compared to off-resonance excitation and to Ag(111) surfaces. The similar (nonthermal) translational energies of desorbed NO in all cases indicate a common mechanism believed to proceed via temporarily trapped hot electrons forming transient negative ions (TNI) which leads to desorption and reaction. Recent results obtained for variable sizes of the AgNP (2 - 10 nm) have shown that characteristics of both thermal and photochemical reactions depend on size. To explain these results, the influences of the size dependences of a number of excitation and decay processes, based on knowledge of the photophysics of the AgNPs, will be discussed. Time permitting, the changes introduced by the use of fs laser pulses will also be presented. These examples show some important consequences of the small dimensions of NMPs, size-dependent confinement effects, and influences of plasmon excitations.

[1] K. Watanabe, D. Menzel, N. Nilius, and H.-J. Freund, Chem. Rev. 106 (2006) 4301.

10:40am **SS2+NC-ThM9 Effects of Nanocluster Surface Chemistry on Electrocatalysis**, ***B.L. Abrams***, *P.C.K. Vesborg, S. Dobrin, D. Mowbray, I. Chorkendorff*, Technical University of Denmark

Nanocluster catalysts in the small size regime (<10nm) offer the opportunity for enhanced catalytic activity due to increased active site availability. This reactivity is also materials dependent and related to how tightly or weakly the nanocatalyst binds the reactants of interest such as hydrogen for the hydrogen evolution reaction (HER).[1,2] Corresponding to the decrease in size is an increase in nanocatalyst surface area. The high surface to volume ratio of nanoclusters in this small size regime thus allows for the ability to impact their catalytic properties by altering their surface chemistry. In this work we alter the cluster surface chemistry by varying the type of surfactants present on metal and metal alloy nanoclusters such as Pt, Au, AuPt, AgPt. These nanoclusters are synthesized using a modified inverse micelle[3] technique where the presence of surfactant molecules (non-ionic or cationic) is crucial to maintaining the nanocluster monodispersity. Following synthesis in the solution phase, the nanoclusters are evaluated electrochemically as a function of surfactant type and amount. In the case of Pt nanoclusters stabilized by a non-ionic surfactant, the HER activity is comparable to standard polycrystalline Pt. The negligible suppression of HER indicates that the surfactant may not significantly block the active sites necessary for HER. In relation to the activity measurements, we have studied the attachment mechanism of the surfactants to the cluster surface utilizing density functional theory (DFT) calculations. An evaluation of the charge transfer processes and reactions as revealed by electrochemical measurements will be presented for each material as a function of surface chemistry alterations. Preliminary result for other reactions of interest to fuel cells such as the hydrogen oxidation reaction will also be discussed.

[1] J.K. Nørskov,et al.,"Trends in the Exchange Current for Hydrogen Evolution" J. Electrochem. Soc. (152), J23 (2005).

[2] Greeley,J.,et al.,"Computational High-Throughput Screening of Electrocatalytic materials for Hydrogen Evolution", Nature Materials, 5,909-913(2006).

[3]Wilcoxon, J.P; Abrams, B.L., "Synthesis, Structure and Properties of Metal Nanoclusters" Chemical Society Reviews, 35,1162-1194(2006).

11:00am **SS2+NC-ThM10 Size-Dependent Structure of $MoS_2$ Nanoclusters**, ***J. Kibsgaard****, *J.V. Lauritsen,* University of Aarhus, Denmark, *S. Helveg, H. Topsoe, B.S. Clausen,* Haldor Topsoe A/S, Denmark, *F. Besenbacher*, University of Aarhus, Denmark

Within the area of nanomaterials it is well know that "small is different", which implies that nanostructures may have new functional properties. Properties like conductivity, color, reactivity, magnetism, and melting point may thus be entirely different for the nanomaterial compared to the same properties for materials with macroscopic dimensions. The dimension of a material is therefore an important parameter to consider in the development of new nanomaterials. Not least in catalysis where the active materials today is confined to a limited number of metals, tuning the size of the catalytic particles may help in the development of new and better catalysts. The $MoS_2$-based desulfurization catalyst constitutes one of the most important environmental catalysts as it removes sulfur from fossil fuels. Without this removal, the sulfur would cause massive acid rain problems such as forest decline. The recent focus on environmental problems and a stricter legislation concerning the sulfur content in fossil fuels have generated great interest in understanding and improving the desulfurization catalyst. We have used atom-resolved Scanning Tunneling Microscopy (STM) to follow the structural progression of triangular $MoS_2$ nanoclusters as a function of their size, and analyse how the equilibrium structures are altered when the cluster size is reduced. A comprehensive analysis of the size distribution reveals that certain "magic" clusters are favored. The analysis reveals that a rearrangement of the sulfur atoms terminating the cluster edges influences the stability and that the requirement to optimize the sulfur excess relative to molybdenum drives a striking reconstruction of the cluster edge.

11:20am **SS2+NC-ThM11 Size-Selected Deposition of Transition Metal Sulfides**, ***M.J. Patterson***, StonyBrook University, *M.G. White*, Brookhaven National Laboratory, StonyBrook University

Supported $MoS_2$ nanoparticles are known for their ability to catalyze a wide array of heterogenous reactions and work done in our laboratory is geared towards understanding the role of size, structure, composition and support interactions of the particles in these reactions. This problem has not yet been resolved due to the inhomogeneity of commercial catalysts. We therefore focus on preparing homogenous samples in ultra high vacuum that can serve as model systems for catalytic reactions such as hydrodesulfurization. A recently constructed cluster beam apparatus in our laboratory uses magnetron sputtering in order to make a variety of transition metal cluster compounds. We are currently investigating the size dependent and substrate dependent properties of these systems in particular $Mo_xS_y^+$ clusters (x=2-8, y= 6-12) on single crystal surfaces (i.e. Au(111), $Al_2O_3$/NiAl(110)). Characterization of the clusters are carried out using surface sensitive techniques such as Auger, photoemission spectroscopy, and thermal desorption. Preliminary work on the reactivity of these clusters with small sulfur containing molecules will also be discussed.

11:40am **SS2+NC-ThM12 Ligand-Spacer Controlled Size Selectivity of Gold Nanoclusters and the Effect of the Ligand on Cluster Geometry and Electronic Structure**, ***G. Shafai***, *S. Hong,* University of Central Florida, *M.F. Bertino,* Virginia Commonwealth University, *T.S. Rahman*, University of Central Florida

We have carried[1] out calculations based on the density functional theory in the projector augmented wave scheme (PAW) and the pseudopotential approach, to examine the effect of the size of the diphosphine ligand spacers on the stability of Au clusters containing 8 and 11 atoms, through evaluations of the cluster total energy and proper correction of spurious interactions between charged supercells. We find that Au11+3 is indeed preferred by ligand L3 rather than L5, while Au8+5 is preferred by L5 rather than L3, in agreement with experimental data.[2] The size selectivity induced by the ligand is found to be a purely electronic effect via coupling of the d-band of Au and p-band of the ligand. We have also examined the effect of the ligand on the geometric and electronic structure of Au clusters. For Au13, for example, we find bare cluster to form a flat flake, in agreement with previous theoretical calculations. On the other hand, Au13 cluster covered with ligands of phosphine (PH3) forms a stable spherical structure (icosahedron), in agreement with experimental findings,[2] which is 0.08 eV lower in energy as compared to the flat-flake complex. If the phosphine is replaced by H, the spherical structure is no longer stable, but it still maintains a 3 dimensional form, signifying the effect of the ligand in stabilization of the structure. We observe a narrow d-band for gold atoms in the flat-flake complex, while in the icosahedron structure the d-band is wider. We also find a stronger overlap between the p orbitals of the P atom with d orbitals of gold atoms in the icosahedron complex.

[1] Work supported in part by by NSF Grant CHE-0741423.

[2] M. Bertino et al. Jour. Phys. Chem. B Lett. 110, 21416 (2006).

## Thin Film
## Room: 302 - Session TF-ThM

## Evaporation, Pulsed Laser Deposition, and Molecular Beam Epitaxy
**Moderator:** J.M. Fitz-Gerald, University of Virginia

8:00am **TF-ThM1 Pulsed Laser Dewetting of Patterned Thin Metal Films: A Means of Directed Assembly**, ***Y.F. Guan***, The University of Tennessee, Knoxville, *J.D. Fowlkes, A.V. Melechko, M.L. Simpson,* Oak Ridge National Laboratory, *P.D. Rack*, The University of Tennessee, Knoxville

One of the challenges of nanoscience and technology is understanding and controlling bottom up directed assembly of materials. A lot of work has been done studying the assembly of continuous thin polymer and metal films which reveal interesting dewetting phenomenon. While the break-up and pattern formation via dewetting of continuous thin metal and polymer films has been studied in detail, less work has been devoted to the dewetting and pattern formation of confined or patterned thin films. In this work, thin nickel films were patterned into various shapes and treated via nanosecond pulsed laser processing. The short liquid lifetimes offers a unique way to monitor the time dependence of the dewetting process and the subsequent pattern formation. Thin nickel films (30 nm) were evaporated onto electron beam lithography patterned PMMA coated (60 nm) silicon substrates. Thin nickel patterns of a variety of sizes of circles, squares, and triangles were achieved by a conventional lift-off process. The edges and vertices of the patterned shapes act as programmable instabilities which enable directed assembly via dewetting when the laser energy density is above the melting threshold. The pattern formations were monitored as a function of laser pulse and the retraction process was attributed liquid dewetting and a subsequent re-solidification. The calculated retraction velocity (83 m/s) and liquid lifetime (12.3 ns) were consistent with the measured nickel retraction distances. The lateral retraction and pattern formation was correlated to a two step process: 1) initially the surface tension drives the flow of the melted nickel films, and 2) a smaller contraction associated with the density difference between the liquid and solid when the liquid film solidifies. The vertices of the shapes had an initially larger retraction velocity which was attributed to an additional in-plane curvature. The reduced retraction rates at subsequent pulses were attributed to thickening of the front which reduces the curvature and enhances viscous dissipation. Acknowledgements: The authors acknowledge support from the Material Sciences and Engineering Division Program of the DOE Office of Science. And a portion of this research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Division of Scientific User Facilities, U.S. Department of Energy.

8:20am **TF-ThM2 Vacancy Ordered Screw Form (VOSF) and Layered Indium Selenide ($In_2Se_3$) Thin Films by Pulsed Laser Deposition**, ***E. Venkatasubramanian***, *F.S. Ohuchi,* University of Washington, *P. Nachimuthu, K.M. Beck*, Pacific Northwest National Laboratory

Indium Selenide ($In_2Se_3$) is an interesting material in the Chalcogenide family and has long been studied owing to its applications in Photovoltaics, optical waveguides and as battery material among others. It has recently garnered even more attention since being demonstrated as a viable phase change memory material with properties that could better GST. Device applications such as these require a film growth technique that is fast, has a high throughput along with the ability to make the desired composition relatively easily. Pulsed Laser deposition is one method that meets all the above criteria and it has also been widely used for making combinatorial samples and thus any optimization study could be done faster. In this work, we report the thin film growth of $In_2Se_3$ by Pulsed laser deposition. Here film deposition was carried out using a 355 nm Nd:YAG laser with a short 5ns pulse width, operating at 20 Hz. Films were subsequently characterized by X-ray diffraction, X-ray photoelectron spectroscopy and Scanning electron microscopy. Both single-phase VOSF and layered $In_2Se_3$ have been obtained exclusively by controlling the deposition conditions and post deposition in-vacuo annealing. The deposited films were found to be uniform and highly oriented along the c-axis. Film stoichiometry and thickness were evaluated by Rutherford Back Scattering and are in accordance with the formula unit and compare well with those obtained from vapor deposited films. Out of plane conductivity measurements were

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* Morton S. Traum Award Finalist

carried out with films deposited on TiN/Si and showed a large difference in conductivity between the amorphous and VOSF phases thereby supporting the use of PLD for growing thin films for Phase Change memory device applications.

8:40am **TF-ThM3 Electrical Conductivity and Thermopower of $Ti_nO_{2n-1}$ Thin Films grown by Pulsed Laser Deposition**, ***N. Nguyen***, University of Washington, *A. Yamamoto*, Advanced Industrial Science and Technology Institute, Japan, *T. Chikyow*, National Institute for Materials Science, Japan, *F.S. Ohuchi*, University of Washington

Reduced titanium dioxide ($TiO_2$) in thin film forms are investigated as a new class of oxide materials for thermoelectric applications. Deposition of thin films was carried out at temperature of 800 °C and oxygen partial pressure of $10^{-7}$ torr on both $SrTiO_3$ (001) and $LaAlO_3$ (001) substrates by pulsed laser deposition (PLD). Initial X-ray diffraction characterizations indicate that thin films are crystallized into a mixture of polycrystalline and texture Magneli phases, $Ti_nO_{2n-1}$ where n = 4, 5, 6… Electrical conductivity ($\Sigma$) and Thermopower (S) of the samples were measured over a temperature range from 10 K to 500 K, from which power factors ($S^2\sigma$) were evaluated as a function of temperature. It was found that $Ti_nO_{2n-1}$ thin films deposited on $SrTiO_3$ yielded unusually large power factors, at room temperature and bellow. These values were at least several times larger than those found on $Ti_nO_{2n-1}$ films deposited on $LaAlO_3$ and typical bulk thermoelectric materials such as $Na_xCo_2O_4$ and $Bi_2Te_3$ at room temperature, and by an order magnitude around T~100K. In addition, the thermopower from thin films deposited on $SrTiO_3$ exhibits large deviation from a small polaron hopping transport mechanism, suggesting that interface defects in a form of oxygen vacancies introduced during PLD play an important role in thermoelectric transport process.

9:00am **TF-ThM4 Effects of Pulsed Laser Deposition Conditions on the Growth of Ge Quantum Dot on Si(100)-(2x1)**, ***A. Er***, *H. Elsayed-Ali*, Old Dominion University

The growth of Ge quantum dots (QD) by pulsed laser deposition of Ge on Si(100)-(2x1) is studied. The samples were first cleaned by using modified Shiraki and IMEC methods and then transferred into the deposition chamber. The vacuum system was then pumped down, baked for at least 12 hours, and the sample was then flashed to 1100 °C in order for the 2´1 reconstruction to form. The experiment was conducted under a pressure ~1x10-9 torr. A Q-switched Nd:YAG laser (wavelength l = 1064 nm) with 10 Hz repetition rate was used to ablate a Ge target. Different substrate temperatures and ablation laser energy densities were used and were shown to affect the quantum dot morphology. In-situ RHEED and ex-situ STM and AFM were used to study the morphology of the grown QD. During deposition, the RHEED patterns changed from elongated streaks to spots. As we increased the ablation laser energy density or the substrate temperature, formation of RHEED spots occurred at less coverage. AFM scans show that the number of clusters and coverage ratio increases with the ablation laser energy density, while the average area of clusters decreases. As we increased the substrate temperature from 400±20 to 500±20 oC, the Ge QD morphology changed from the asymmetric hut shape to the symmetric dome shape. Also, a decrease in the number of clusters and coverage ratio was observed.

9:20am **TF-ThM5 Unique Initial Growth Mode for Rare-Earth Group-V Nanocrystals on III-V Semiconductors**, ***S.G. Choi***, *Y. Yan*, National Renewable Energy Laboratory, *B.D. Schultz*, International Technology Center, *C.J. Palmstrom*, University of California, Santa Barbara

Incorporation of rare-earth group-V (RE-V) compounds into III-V semiconductors has generated considerable interests as a result of their potential applications in thermodynamically stable metallic contacts to III-V semiconductors and metal-based novel electronic devices. It has recently been demonstrated that RE-V's in a nanocrystal (NC) form embedded in III-V semiconductor matrix can extend their applications to advanced photonic devices and high-efficiency thermoelectric devices.[1,2] High device performance relies upon the synthesis of heterostructures in a controlled manner, and therefore a good understanding of the structure for the growth front is of great importance. Even though early growth studies have shown that the formation of RE-V's on III-V semiconductors is not associated with any of the typical growth modes, details of their unique growth nature were not discussed until recently.[3,4] Our in-situ surface studies on ErAs/GaAs[3] and ErSb/GaSb[4] systems suggest that the incoming Er atoms displace the Ga atoms in the substrate and form ErAs and ErSb nanocrystals "within" the substrate surface rather than on top. After 3 – 4 monolayers deposition, RE-V NCs form a continuous layer and then grow via "layer-by-layer" modes for the remaining growth. We have used cross-sectional high-resolution High Angle Annular Dark Field Scanning Transmission Electron Microscopy (HAADF-STEM) to study the ErSb NC formation as a result of 1 monolayer ErSb deposition on molecular beam epitaxially grown GaSb(001) surfaces. The HAADF-STEM studies clearly show the formation of ErSb NCs "within" the GaSb substrate surface consistent with the in-situ surface science studies and the embedded growth model.[3,4] In this presentation, we will correlate ex-situ cross-sectional HAADF-STEM results with in-situ reflection high-energy electron diffraction, low-energy electron diffraction, x-ray photoemission spectroscopy, and scanning tunneling microscopy studies to determine the unique formation mechanism involved during the growth of ErAs and ErSb NCs in III-V semiconductors. This work was supported in part by ARO and NSF-MRSEC. This abstract is subject to government rights.

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9:40am **TF-ThM6 Growth and Characterization of Cuprous Oxide Nanoclusters on Strontium Titanate (100) Surface**, ***S.V.N.T. Kuchibhatla***, Pacific Northwest National Laboratory, *Z.Q. Yu*, Nanjing Normal University, China, *S. Thevuthasan, P. Nachimuthu, V. Shutthanandan, C.M. Wang, Y. Li, C.H. Henager, Jr., S.K. Sundaram*, Pacific Northwest National Laboratory

Growth of electronic materials as single crystals for a variety of uses can be limited by the lack of fundamental understanding of the nucleation, growth, and coalescence regime at the initial stages of the growth process. As a first step in comprehensively developing a knowledge database on the nucleation and growth of various materials, we have investigated the growth of cuprous oxide ($Cu_2O$) nanoclusters on $SrTiO_3$(100) substrate. There has been considerable interest in $Cu_2O$ nanoclusters because they can be used effectively in chemical and photochemical applications due to their unique electronic transport properties. We have grown $Cu_2O$ clusters using oxygen plasma assisted molecular beam epitaxy (OPA-MBE) and the effects of deposition rate, substrate temperature, oxygen pressure, and deposition time were systematically studied. Structural, morphological, and chemical properties of these clusters were investigated using several surface and bulk interrogation methods. X-ray diffraction (XRD) and x-ray photoelectron spectroscopy (XPS) measurements clearly demonstrated the complex nature of the copper oxide system due to the possibility of co-existing Cu(0), Cu(1), and Cu(2) phases in the clusters. Optimum deposition conditions were established to produce pure $Cu_2O$ clusters. Atomic force microscopy (AFM) images clearly showed the growth of uniformly distributed epitaxial, faceted pure $Cu_2O$ clusters on STO (100) with (100) orientation. Rutherford backscattering spectrometry (RBS) measurements have been used along with the AFM and transmission electron microscopy (TEM) measurements to compute the thickness of the films. The cluster size, shape and their preferred orientation were critically analyzed. It is observed that the surface morphology, cluster coalescence, and film formation are highly dependent on various growth parameters including growth rate, deposition temperature, and deposition time. Theoretical investigations have also been carried out to understand growth mechanisms and these results will be presented along with the experimental observations.

10:40am **TF-ThM9 Low Temperature Growth of High-Quality Indium Nitride on Si(100) by Femtosecond Pulsed Laser Deposition**, ***M.A. Hafez***, *H. Elsayed-Ali*, Old Dominion University

The growth and structural properties of indium nitride (InN) grown on Si(100) substrates by femtosecond pulsed laser deposition (fsPLD) are studied. Deposition InN on Si(100) is performed with an amplified Ti:sapphire laser (130 fs) at wavelength of 800 nm. Laser induced gas breakdown-assisted PLD is used to generate reactive nitridation from ammonia. Prior to InN growth, an intermediate two-dimensional layers of indium on Si(100) surface at substrate temperature of ~70 $^{o}$C is performed by fsPLD under ultrahigh vacuum (low $10^{-9}$ Torr). In situ reflection high-energy electron diffraction (RHEED) is used during the deposition to monitor the structure and morphology of the film growth. The InN films are prepared at room temperature to a substrate temperature of ~350 $^{o}$C. The grown films are examined by ex situ atomic force microscopy, scanning electron microscopy, and x-ray diffraction (XRD). RHEED and XRD analysis showed high-quality InN films grown on Si(100). The quality and structural properties of the InN films are improved by employing a low-temperature buffer layer and by the nitridation process. RHEED observation showed that InN grew on Si(100)-(2x1) surface by the Stranski-Krastanov mode. The growth mode and morphology of the InN films is influenced by the surface condition of Si(100) substrate. The kinetic effect of the PLD has a main rule in improving the initial layers and the formation of InN. The obtained results demonstrate the potential of the growth procedure for deposition of high quality InN epitaxial layers by fsPLD at reduced temperatures.

11:00am **TF-ThM10 Thin Films by Metal-Organic Precursor Plasma Spray**, ***D.L. Schulz***, *R.A. Sailer*, North Dakota State University, *J. Leach, R. Molz*, Sulzer Metco (US)

While most plasma spray routes to coatings utilize solids as the precursor feedstock, metal-organic precursor plasma spray (MOPPS) is an area that we have investigated recently as a novel route to thin film materials. Very thin films are possible via MOPPS and the technology offers the possibility of forming graded structures by metering the liquid feed. To date, liquid-based precursor plasma spray efforts have utilized solutions of metal salts or dispersed colloidal particles with a limitation of these approaches related to the fact that most of the plasma energy is expended toward evaporation/combustion of the solvent which starves this process of the energy required to promote film formation. The current work employs metal-organic compounds that are liquids at standard temperature-pressure conditions. In addition, these complexes contain chemical functionality that allows straightforward thermolytic transformation to targeted phases of interest. Toward that end, aluminum sec-butoxide (Al(OBu)3) and aluminum 3,5-heptanedionate (Al(hd)3) were used as precursors to alumina while triethylsilane (HSi(C2H5)3) and titanium tetrakisdiethylamide (Ti(N(C2H5)2)4) were employed for studies toward silicon carbide and titanium-nitride-carbide. In all instances, the precursors contain metal-heteroatom bonds envisioned to provide atomic concentrations of the appropriate reagents at the film growth surface thus promoting phase formation (e.g., Si-C bond in triethylsilane, Ti-N bond in titanium amide, etc.). Films were deposited using a Sulzer Metco Triplex Pro-200 Plasma Spray system under various experimental conditions using Design of Experiment (DoE) principles. The composition and morphology of these films was studied as a function of application conditions. Film compositions were analyzed by glancing incidence x-ray diffraction (GXRD) and elemental determination by x-ray spectroscopy (EDS). Silicon carbide and titanium-nitride-carbide films typically exhibited a continuous morphology with reasonable adhesion (i.e., passed tape pull adhesion test) while aluminum oxide films ranged from powdery to continuous but suffered from poor adhesion.

11:20am **TF-ThM11 Dependence of Fiber Texture on Composition in Au-$SiO_2$ Composite Thin Films**, ***D.I. Filoti***, *A.M. Brown, D. Carlson, J.M.E. Harper*, University of New Hampshire

We show that the evolution of metal fiber texture in sputtered metal-insulator composite thin films depends strongly on the composition through the presence of second-phase particles that interrupt normal metal grain growth. Using x-ray diffraction pole figures, we measured the strength of the Au(111) fiber texture as a function of composition in the Au-$SiO_2$ system, which phase segregates during deposition. For very low $SiO_2$ volume fractions less than 0.05, the Au has low resistivity and a strong (111) fiber texture similar to that of pure Au. For higher $SiO_2$ volume fractions up to 0.3, the strength of the fiber texture decreases rapidly with increasing volume fraction of $SiO_2$ second-phase particles, and the resistivity increases. For $SiO_2$ volume fractions greater than 0.3, the fiber texture is lost as the Au becomes discontinuous and the microstructure changes to randomly oriented Au islands within an insulating matrix of $SiO_2$, confirmed by resistivity and transmission electron microscopy measurements. We show that the rapid decrease in Au(111) fiber texture strength correlates with a reduction in Au grain size caused by Zener pinning of Au grains by second-phase $SiO_2$ particles. Grain boundary pinning by second-phase particles prevents the development of (111) fiber texture that usually occurs during normal grain growth. The result is a more rapid loss of fiber texture as a function of composition than can be explained only by the decreasing Au volume fraction.

11:40am **TF-ThM12 Phase Transformation Behaviors of $SiO_2$ Doped $Ge_2Sb_2Te_5$ Films for Application in Phase Change Random Access Memory**, ***S.W. Ryu***, *J.H. Lee, Y.B. Ahn, C.S. Hwang, H.J. Kim*, Seoul National University, South Korea

Phase change random access memory (PCRAM) has attracted a great interest because it satisfies various demands for nonvolatile memory devices.[1-3] PCRAM uses the reversible phase change between the crystalline and amorphous states of chalcogenide materials, such as $Ge_2Sb_2Te_5$ (GST), brought about by Joule heating. However, the high level of $I_{res}$ has been the major obstacle to the further scaling of PCRAM because of the limited on-current drive capability of the cell transistor (<0.5 mA/μmm). There have been several reports on the improvement of the switching performance of GST achieved by doping it with various impurities, such as N,[4] O,[5] Si,[6] or $SiO_2$.[7] In the case of $SiO_2$ doped GST (S-GST), it was reported that the reset current is reduced by approximately 50% compared to that of undoped GST. [12] The improvement in the phase change characteristics of GST films was investigated by doping the GST films with $SiO_2$ using cosputtering at room temperature. As the sputtering power of $SiO_2$ increased from 0 to 150 W, the activation energy for crystallization increased from 2.1±0.2 to 3.1±0.15 eV. $SiO_2$ inhibited the crystallization of the amorphous GST films, which improved the long term stability of the amorphous phase. The melting point decreased with increasing concentration of $SiO_2$,which reduced the power consumption as well as the reset current.

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## Tribology Focus Topic
## Room: 205 - Session TR+SE+TF-ThM

## Advances in Surface Engineering for Friction and Wear Control

**Moderator:** K.J. Wahl, U.S. Naval Research Laboratory

8:00am **TR+SE+TF-ThM1 Evaluation of Ti-In-N Films for Tribological Applications**, ***J.E. Krzanowski***, *M. Nowicki*, University of New Hampshire

Titanium nitride and indium have both found applications as tribological coatings. While TiN is used primarily for its high hardness and wear resistance, indium can be used as a solid lubricant layer. In this study, we have examined the concept of using co-deposited TiN-In films for tribological applications. Ti-In-N films have been deposited by RF co-sputtering of Ti and In in a nitrogen/argon atmosphere. By varying the power to the Ti and In sources, the In/Ti ratio in the film was varied. Films were deposited at DC substrate bias levels of -50V and -150V. In both cases, as the In/Ti power ratio was increased, the indium content increased, but in a highly non-linear manner. At lower power ratios, the films had a cubic TiN structure, but as the power ratio increased, there was an abrupt transition to a hexagonal structure. Near the transition point, the films could also be amorphous, depending on film thickness, and thicker films were more likely to be crystalline. Below the transition point, the film composition depended strongly on substrate bias, and films deposited at -150V bias exhibited significantly reduced indium contents. Tribolgical tests were conducted using a pin-on-disk test with an alumina counterface. Most films showed shorter wear lives compared to TiN alone. The friction coefficients were found to depend on the In content in the films, and it was also found that heating films for short times in the range of 100-250C reduced friction coefficients.

8:20am **TR+SE+TF-ThM2 Nanostructured Sulfur Doped CHx-TiB2 Coatings for Improved Mechnical and Friction Performance**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films results in ultra-low friction performance in both dry and humid environments. However, these films have a hardness of 7 - 10 GPa and an elastic modulus around 80 GPa, which are too low for some high stress applications. Formation of nanostructured coatings is known to improve hardness. With the aim to produce hard, low-friction coatings, we synthesized nanolayered and nanocomposite films of sulfur-doped hydrogenated carbon and titanium diboride using dual-target magnetron sputtering. Titanium diboride deposited by this method had a hardness >30 GPa. This paper will discuss the film structure and how such structure correlates with its tribological and mechanical properties.

8:40am **TR+SE+TF-ThM3 Latest Developments on the Family of C-alloyed TMD Self-lubricating Coatings**, ***A. Cavaleiro***, SEG-CEMUC - University of Coimbra, Portugal, *T. Polcar*, CTU Prague, Czech Republik, *M. Evaristo*, SEG-CEMUC - University of Coimbra, Portugal **INVITED**

Due to their layered structure and weak inter-layer bonding, transition metal dichalcogenides (TMD) exhibit very interesting physical and tribological properties. Among different TMD families (TmS2, TmSe2 and TmTe2, with Tm = Mo, W, Nb) MoS2 and WS2 have been the most intensively studied in last decades. They are now currently used either as oil additives or as thin self-lubricating coatings. The industrial applicability of these coatings is still very limited owing to their two main drawbacks: (1) the loss of the tribological performance in humidity-containing environments and, (2) the low load bearing capacity. Several solutions have been proposed to overcome these problems as, for example, alloying TMD coatings with other elements or compounds, such as C, Ti, Pb, and TiN. The concept of coatings based on TMDs alloyed with carbon was introduced in the 90´s and was based on the expected synergy between the excellent frictional behavior of TMD in vacuum/dry air and the tribological performance of C-based materials. Improved frictional performance of the W-S-C coatings could be achieved when the coatings were tested by environmental cycling from dry to humid air (FC - friction coefficient from 0.02 to 0.15). Successive changes in the sliding mechanisms based on the modification of the contact layers were assigned as responsible for this behaviour. The TMD+C solution was adopted by the authors for their research by studying its extension to other TMD-C systems. The aim of this talk was to present the latest developments achieved within TMD-C magnetron sputtering deposited coatings concerning di-selenides (Mo-Se-C and W-Se-C). Lower friction coefficient was achieved in comparison to previous deposited W-S-C coatings, particularly in humid air. FC was possible to be kept lower than 0.05 in all testing conditions. Tests were performed with contact stress as high as 1.5 GPa without destruction of the coating. The frictional and wear mechanisms under different operating conditions were studied by nanoscale analysis of the wear tracks. The tribological performance, whatever the testing conditions, was attributed to the formation of a thin tribolayer consisting exclusively of TMD platelets with the (002) plans oriented parallel to the sliding motion. C is removed from the contact area during the re-orientaion process, only playing a secondary role by increasing the coatings density, avoiding surface oxidation and improving the loading bearing capacity.

9:20am **TR+SE+TF-ThM5 Reduction in Friction and Micropitting by Coatings and Lubricants Containing Inorganic Fullerenes**, ***S.J. Bull***, *A. Oila*, Newcastle University, UK

Improvement in component performance by reduction in friction and wear has been the focus of considerable research over the last forty years. As products become more highly engineered and component size is reduced the significance of friction and wear is increased, particularly in terms of improvements in energy efficiency, and the need to develop materials with improved triboloigcal performance becomes critical. Nanostructured materials are one way whereby this might be achieved. Recent work has focussed on the development and assessment of nanomaterials and composites for triboloigcal performance. In particular, the use of inorganic fullerene-like materials in the form of coatings and nanoparticles (and as the reinforcement for nanocomposites) has shown a lot of promise for tribological applications. This talk will highlight the use of inorganic fullerene nanoparticles as additives for lubricating oils or coatings to achieve a significant increase in the operational life of rolling/sliding components such as gears.

9:40am **TR+SE+TF-ThM6 Tribology of Carbon Films in Hydrogen and Deuterium Gas Environments**, *A. Erdemir*, ***O.L. Eryilmaz***, Argonne National Laboratory

Recent systematic studies in our laboratory have shown that certain diamond-like carbon (DLC) films are able to achieve superlow friction and wear when tested in hydrogen-containing test environments. In the presence of deuterium, we were also able to achieve very low friction and wear on these films. In this study, we used a combination of controlled-environment atmospheric pressure and vacuum tribometers to further verify the critical effects of hydrogen and deuterium on friction and wear of such films; then we used imaging SIMS and XPS methods to ascertain the near surface chemistry of their sliding surfaces. The combined results of tribological tests and surface analytical studies revealed that there exist a close correlation between the chemical nature of sliding DLC surfaces and their friction and wear behaviour. Specifically, we found that in the presence of both hydrogen and deuterium, the sliding contact areas of carbon films were covered by a hydrogen and deuterium film (only a few Å thick). The wear rates and friction coefficients are much higher if tests were run in dry nitrogen or vacuum than in hydrogen and deuterium. Overall, we show that superlow friction behaviour of certain DLC films is largely controlled by gas-surface interactions.

10:40am **TR+SE+TF-ThM9 Tribomaterials for Spacecraft: Testing & Surface Chemistry**, ***J.R. Lince***, The Aerospace Corporation **INVITED**

The spacecraft environment is challenging for tribocoatings and lubricants used in devices in satellites and launch vehicles. Areas of concern include vibration during launch, thermal cycling on orbit, and the need to work effectively for missions up to twenty years in duration without lubricant replenishment. Especially challenging is the need for tribomaterials to withstand the vacuum of space during lengthy missions. Spacecraft tribomaterials must exhibit low vapor pressures, since evaporation of lubricants can result in loss from and premature failure of devices, as well as contamination of sensitive spacecraft components. A relatively small set of liquid lubricants meet the vapor pressure requirement – while also meeting performance requirements for current spacecraft applications – including synthetic hydrocarbons and perfluorinated polyalkylethers. Soft solid lubricants such as molybdenum disulfide ($MoS_2$) and polytetrafluoroethylene (PTFE) have been used traditionally. More recently, hard low friction coatings such as hydrogenated diamond-like carbon have shown promise for operation in vacuum with existing spacecraft lubricants, or even unlubricated operation in vacuum. These solid- and liquid-based tribomaterials show performance in vacuum that differs with that in air, nitrogen, or even with small partial pressures of oxygen and water. This is especially important for spacecraft hardware, because it is often prohibitive to test them in a space-like environment, including vacuum, before launch. As such, differences between non-vacuum and vacuum testing need to be understood in order to predict how lubricated devices will perform in space. This talk will focus on a series of recent studies done at The Aerospace Corporation that elucidate the effects of vacuum and other environments on the tribological performance of several important spacecraft tribomaterials. The emphasis will be on how varying environments affect the surface chemistry of the materials.

11:20am **TR+SE+TF-ThM11 Nano-Smooth Diamond Coatings on Various Alloys for Ultralow Friction in the Presence of OH-Containing Lubricants**, ***T. Gries***, CNRS - ICARE, France, *C. Matta, M.I. De Barros Bouchet, B. Vacher*, Ecole Centrale de Lyon, France, *S. de Persis*, ICARE - CNRS, France, *L. Vandenbulcke*, CNRS, France

Titanium alloys and titanium-coated alloys are important materials for aerospace, mechanical, chemical and biomedical applications; however their applications could be extended by improving their tribological behaviour. This can be done by using diamond-based coatings which are outstanding materials for changing their surface properties. We have shown that nano-smooth fine-grained diamond coatings could be deposited on these alloys at moderate temperature, equal to or lower than 600°C, from $CH_4$-$CO_2$ species. They are in fact duplex coatings with an external diamond film, a titanium carbide sub-layer and a diffusion solid-solution. These coatings exhibit particularly strong adherence with the substrates as shown by various mechanical tests and very high induced stresses without peeling off. They are first described in terms of $sp^2$-hybridized carbon contents relatively to the $sp^3$-carbon ones, a parameter which influences the structure and the intrinsic diamond properties (surface roughness in the 15-35 nm range, micro-hardness, Young's modulus and residual stresses). The whole is correlated to the plasma enhanced CVD process through the formation of different concentrations of the gaseous precursors in the plasma which include both radicals and stable species as revealed by molecular beam mass spectrometry and corroborated by kinetic calculations in the C-H-O plasmas. These coatings are studied by micro-Raman spectroscopy and their structure is revealed by TEM studies. A $sp^2$-C enriched layer is especially evidenced at their extreme surface by Energy-Filtered TEM on transverse cross-sections, a layer which is important for tribochemical reactions. While the friction coefficient is high under ultra high vacuum, ultra low friction is obtained in saline corrosive solution. Ultra low friction with no wear is also obtained with gas phase lubrication by glycerol under boundary lubrication regime, in conditions which permit a better identification of the friction mechanism from advanced surface characterizations. These studies allow concluding that lubrication of these diamond coatings by OH-containing molecules can permit new or improved applications in various fields. Some examples of ultra low friction and low wear are provided when nano-smooth diamond coatings or alumina are sliding on nano-smooth diamond in corrosive saline solution or in the presence of glycerol lubricant, a model of environmentally friendly molecules.

11:40am **TR+SE+TF-ThM12 Tribology of Nanocrystalline Diamond Coatings**, ***N.D. Theodore***, North Carolina State University, *K.J. Wahl*, Naval Research Laboratory

The tribological behavior of several nanocrystalline diamond (NCD) coatings was compared to correlate compositional, structural, and chemical bonding differences to their friction performance. The diamond coatings were confirmed by X-ray diffraction (XRD) to be nanocrystalline with crystallite sizes ranging from to 4 to 60 nm. These diamond coatings could be differentiated from each other by their visible wavelength Raman absorption bands. Some coatings had a single strong peak at 1332 $cm^{-1}$ typical of crystalline diamond bonding; others also had broad peaks at 1340 $cm^{-1}$ and 1580 $cm^{-1}$ characteristic of the D and G peaks in $sp^2$ hybridized carbon; and still others had additional peaks at 1135 $cm^{-1}$ and 1470 $cm^{-1}$, which are commonly attributed to polyacetylene bonding. Reciprocating sliding tests using diamond counterfaces in controlled humidity environments resulted in low friction values for all coatings, between 0.02 and 0.09. The coatings exhibiting lower friction values possessed lower mean surface roughnesses, as measured using an atomic force microscope (AFM), smaller crystallite sizes, and increased amounts of non-$sp^3$ carbon content. Transmission Fourier transform infrared (FTIR) microscopy was used to examine the bonding chemistry in the coatings and wear tracks. The role of diamond coating microstructure, surface roughness, and bonding chemistry to the tribological behavior of NCD will be presented.

# Thursday Morning, October 23, 2008

## Exhibitor Workshops
## Room: Exhibit Hall - Session EW-ThM

## Exhibitor Workshops
**Moderator:** R.A. Childs, MIT

10:00am **EW-ThM1 SPR Imaging in Biosensor Development**, *V. Kodoyianni*, ***T.G. Burland***, GWC Technologies Inc.

Surface biosensors have potentially broad applications in areas ranging from research to diagnostics to environmental testing, among others. Rapid increases in our knowledge of protein biology, together with increases in protein engineering capabilities, are expanding the opportunities to develop useful biosensor devices. However, implementing surface sensors based on proteins can be challenging, as a given surface immobilization method can have profoundly different impacts on the activity of different proteins. We will present examples of how SPRi (Surface Plasmon Resonance Imaging) can be used as a tool to identify and solve surface sensor fabrication problems, and how such sensors can be used to detect a wide range of biological targets.

## 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, ***Z. Liu***, University of California, San Diego **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 receive 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.

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 nano-composite 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 32oC. 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. Sebba, 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. Schvartzman***, *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 oC 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 fluorescene 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 use of ease. 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 formion 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 re-dispersal 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 $H_2N$-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. Bottenus, 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 $SiO_2$ 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 $SiO_2$ 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: $7mm^2$; 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.

[1] F. Schreiber, Prog. Surf. Sci. 65, 151 (2000)

[2] G.L. Kenausis et al., J. Phys. Chem. B 104, 3298 (2000)

[3] S. Pasche et al., Langmuir 19, 9216 (2003).

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 μmg/ml, the protein forms a monolayer with a density of 112 ± 4 ng/cm$^2$ 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.

## Electronic Materials and Processing
## Room: 210 - Session EM-ThA

### Organic Electronics
### **Moderator:** R.L. Opila, University of Delaware

2:00pm **EM-ThA1 Dependence of Contact Resistance and Field-Effect Mobility on Morphology in Poly(3-hexylthiophene based Field-Effect Transistors**, ***K.A. Singh****, G. Sauvé, R. Zhang, T. Kowalewski, R.D. McCullough, L.M. Porter*, Carnegie Mellon University

The field-effect mobility and the contact resistance (Rc) of field effect transistors (FETs) based on regioregular poly(3-hexylthiophene) (P3HT) were investigated as a function of the molecular weight (Mw). Bottom-contact FETs were fabricated having Pt or Au contacts with the channel lengths varying from 3 to 40 μm. Our electrical measurements show an initial increase (decrease) of the mobility (contact resistance) with Mw followed by a saturation of the values. For example, at a gate voltage of -80V and for Mw between 5.5 and 11 kDa in FETs with Pt contacts, the mobility increased from 0.05 to 0.16 cm$^2$V$^{-1}$s$^{-1}$, whereas the contact resistance decreased from 1.7 to 0.5 MΩ. However, above 11 kDa, the values remained relatively constant. Devices with Au contacts displayed a similar trend, although the mobilities were lower and the contact resistances were higher, as expected due to the lower work function of Au. The inverse relationship between mobility and Rc is attributed to the dependence of Rc on bulk transport through a depletion region associated with defects near the contacts.[1] Atomic force microscopy (AFM) images indicate that P3HT self assembles in a nanofibrilar morphology.[2] It is also evident that an increase in Mw leads to an increase in the width of the self-assembled nanofibrils and, at the highest molecular weights, to a simultaneous disruption arising from folding of the polymer chains. An associated loss in conjugation within the polymer chains, along with a possible disruption in the π-π stacking that occurs concurrently with the increase in nanofibril size, would account for the saturation of the mobility and the contact resistance at higher molecular weights. In summary, our results show that mobility and contact resistance in P3HT-based FETs depend strongly on the polymer nanomorphology and display an inverse relationship with each other, supporting the theory that the contact resistance is affected by the bulk transport properties of P3HT. Future experiments including X-ray scattering studies are planned to further quantify the structure within the P3HT films.

[1] L. Bürgi, T. J. Richards, R. H. Friend, and H. Sirringhaus, J. Appl. Phys. 94[9], 6129(2003).

[2] R. Zhang, B. Li, M.C. Iovu, M. Jeffries-EL, G. Sauvé, J. Cooper, S. Jia, S. Tristram-Nagle, D.M. Smilgies, D.N. Lambeth, R.D. McCullough, and T. Kowalewski, J. Am. Chem. Soc. 128[11], 3480(2006).

2:20pm **EM-ThA2 In-Situ Characterization of the Thermal Transformations of High Performance Polymer Semiconductors**, ***L.J. Richter****, A.J. Moad, D.M. DeLongchamp, R.J. Kline, D.A. Fischer, D.J. Gundlach, B.H. Hamadani,* National Institute of Science and Technology, *M. Heeney, I. McCulloch*, Imperial College London, UK

Polymer semiconductors are inexpensive solution processable alternatives to amorphous silicon for applications in flexible large area electronics. Recently, thin films of spun-cast poly(2,5-bis(3-alkylthiophen-2yl)thieno[3,2-b]thiophene) (pBTTT) have been demonstrated to exhibit exceptional hole mobilities in thin film transistors (TFTs) after heating into a low temperature (~ 150 °C) mesophase. This mild thermal cycle results in high level of crystalline order in the annealed film with a morphology exhibiting single molecular layer terraces. Recently we have discovered that heating into a second, higher temperature (~240°C) phase results in a distinct ribbon morphology. The ribbon phase can be oriented over large (cm$^2$) areas by a simple flow coating process. We have applied polarized optical spectroscopies: spectroscopic ellipsometry and FTIR, along with x-ray diffraction and NEXAFS to the in-situ study of the structural evolution in the two high temperature phases. The first mesophase is a well ordered liquid crystal characterized by melted side chains, but excellent vertical lamella order. The second, high temperature phase appears to be an isotropic melt. The behavior of pBTTT is contrasted with that of poly(dialkylthieno[3,2-b]thiophene-2,5-bithiophene) (pTTBT), a newly synthesized isomer of pBTTT with side chains attached to the thienothiophene rather than the bithiophene unit. This subtle structural change results in distinct thermal behavior. The structural transitions of the isomers are generally similar; however, the side chain melting transition Tm occurs about 50°C lower in pTTBT than in pBTTT. The significant drop in Tm appears to correlate with a subtle decrease in main chain packing interactions. Both materials exhibit high hole mobility, even in their respective liquid crystal mesophases. The slight overall higher order in pBTTT is reflected in the annealed device performance.

2:40pm **EM-ThA3 Advances in Plexcore™ Active Layer Technology Systems for Organic Solar Cells**, ***S.P. Williams****, D.W. Laird, S. Li, J. Bernkopf, S. Jia*, Plextronics, Inc.

Abstract: Plextronics designs and develops active layer technology for printed electronics devices - OLED displays and lighting, polymer solar cells and plastic circuitry. Active layer technology is the printed semiconductors and conductors that drive device performance. Plextronics has robust control of polymer design and ink formulation, as well as an intimate understanding of device physics and its impact on device performance. This knowledge is applied to the creation of Plexcore™ technology. Plexcore technology is designed to maximize the efficiency, lifetime and stability of printed electronic devices. This talk will emphasize advances to our Plexcore™ PV technology system for Organic Solar Cells. This active layer system includes the hole-transport layer (HTL), and the p-type and n-type semiconductors. To date, Plexcore™ PV has achieved world-class NREL certified efficiency for an all-organic solar cell at 5.4%. In addition, we will discuss both advances in both materials and device properties/performance, OPV cell lifetime measurement and performance, and our trajectory toward commercialization.

3:00pm **EM-ThA4 Isolation of Aging Components in Organic Transistors**, ***J.E. Royer****, J. Park, C.N. Colesniuc, F. Bohrer, A. Sharoni, I.K. Schuller, W.C. Trogler, A.C. Kummel*, University of California, San Diego

A systematic approach to isolating the cause of device degradation ("aging") in copper phthalocyanine (CuPc) organic thin film transistors (OTFTs) is presented. Aging is one of the primary impediments to the widespread deployments of OTFTs in gas sensors and as drivers for OLEDs. Exposure of 1000ML thick CuPc OTFTs to a sequence of environments including ambient air, clean dry air (20% $O_2/N_2$), water vapor and $N_2$ isolated the causes of device degradation in thick CuPc OTFTs. Initial exposure to ambient air increases conductivity of the CuPc film but also causes rapid device aging characterized by increased threshold voltage and loss of saturation behavior consistent with a loss of control of the channel conductivity by the gate. Exposure of the thick CuPc OTFTs to clean dry air, $H_2O/N_2$ mixture, or clean air/$H_2O$ mixture not only prevents aging but can counter the aging effect of ambient air. This suggests that $O_2$, $H_2O$ and $O_2/H_2O$ products are not responsible for the aging process in ambient air. The data is consistent with trace strong oxidants in ambient air (e.g. $O_3$ and $NO_x$) being responsible for OTFT aging via formation of fixed charge. The aging effect is only present in thick films and is attributed to strong oxidants dissociative chemisorbing in grain boundaries to form fixed charges which degrade the control of the OTFT conductivity by the gate.

3:20pm **EM-ThA5 Modification of Transport Levels of Organic Single Crystals Functionalized with Self Assembled Monolayers**, ***A.S. Wan***, *S. Rangan, D.D.T. Mastrogiovanni, E. Bersch, B. Lee, S. Katalinic, M. Connors, E. Garfunkel, R.A. Bartynski, V. Podzorov*, Rutgers University

We present the first detailed study of energy level modification of single crystal organic semiconductors by functionalization with self-assembled monolayers (SAMs) deposited from the vapor phase by combined photoemission and inverse photoemission spectroscopy (PES-IPES). Large changes in conductivity in organic crystal transistors are observed between pristine and functionalized surfaces. For example, in the case of rubrene functionalized with fluorinated trichlorosilane (FTS) SAMs the conductivity increases almost 6 orders of magnitude at full coverage.[1] Preliminary evidence suggests that the presence of electron-withdrawing SAM on the organic crystals acts to p-type dope the surface, which could lead to the observed energy level and conductivity changes. X-ray photoemission (XPS) results examining both the band bending in the bulk of the organic crystals as well as interface chemistry, as well as scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) will also be discussed.

[1] M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson, and V. Podzorov. Nat. Materials 7, 84 (2008).

4:00pm **EM-ThA7 Ion Scattering Studies of Self-Assembled Monolayers Grown on Organic Molecular Single Crystals and Polymers**, ***L.S. Wielunski***, *S. Katalinic, B. Lee, V. Podzorov, E. Garfunkel, L.C. Feldman*, Rutgers University

It has been recently observed that electrical conductivity of small-molecule organic semiconductors (such as Rubrene) can be strongly enhanced in the presence of fluorinated silane SAM at the surface.[1] In order to understand the microscopic origin of this large electronic effect and to resolve the exact SAM composition, we have performed Rutherford Backscattering Spectrometry (RBS) of SAM-rubrene and SAM-polymer systems using 2 MeV He ions. RBS allows a determination of the fluorine and silicon concentrations in a monolayer-thick film formed at the surface of organic crystals and polymers. Preliminary results indicate a modified SAM composition upon adsorption, possibly due to new interfacial chemistry or possibly due to beam induced effects. The analytical results will be compared with electrical measurements of SAM-induced conductivity in organic semiconductors.

[1] M. F. Calhoun, J. Sanchez, D. Olaya, M. E. Gershenson and V. Podzorov, Nature Mat. 7, 84 (2008).

4:20pm **EM-ThA8 Soft X-Ray Spectroscopic Studies of the Electronic Structure of Cu(tfacac)$_2$en (TFAC)**, ***A. DeMasi***, *L.F.J. Piper, R. Allenbaugh, L. Doerrer, K.E. Smith*, Boston University

The valence and core level electronic structure of the organic molecule Cu(tfacac)$_2$en, or TFAC, has been measured using synchrotron radiation-excited resonant x-ray emission spectroscopy (RXES) and x-ray photoelectron spectroscopy (XPS). Samples were in the form of thin films, grown in-situ in an organic molecular beam deposition chamber attached to the spectrometer system. The thin films were characterized with scanning electron microscopy (SEM) after growth, and ordering is observed that is consistent with expectations for molecular beam deposition. The films were found to be sensitive to photon induced beam damage, but this problem could be alleviated by continuous translation of the films during measurement. Our measurements indicate that TFAC potentially has semiconducting properties, and may compare favorably with copper phthalocyanine as an organic semiconductor. Work supported in part by the AFOSR.

## 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. Miiller***, 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, ***S. Chen***, Massachusetts Institute of Technology **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-indentor, 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.

[1] J.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.

[1] A P Merkle and L D Marks. "Friction in Full View." Applied Physics Letters 90, 064101 (2007).

[2] Y Liu, A Erdermir, 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) pro-vided 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 envi-ronment, 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 1500oC, 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 $TiO_2$ 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 $CO_2$ 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 $TiO_2$ 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 ($TiO_2$) nanoparticles during annealing in vacuum at temperatures up to 1000 oC. First, C-coated titania particles are prepared by pyrolysis of propylene ($C_3H_6$) 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 ~ $10^{-6}6$ 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 $TiO_2$; 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 $TiO_2$ 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 posses 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 $H_2S$ 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 microcystallites, 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:$Y_2O_3$ nanotubes (NTs) and nanoparticles (NPs) and Er:$La_2(Zr_xHf_{1-x})_2O_7$ 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 spectroscopy[3] to be single crystalline, with well controlled size distributions around 100-400 nm in outer diameter and 2-5 μm in length for Er:$Y_2O_3$ NTs, around 80 nm in diameter for Er:$Y_2O_3$ NPs, and around 15 nm in diameter for Er: $La_2(Zr_xHf_{1-x})_2O_7$ 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 $Y_2O_3$ 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).

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

## 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/in$^2$ 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 um 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 multi-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 nano-scale 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-templaed 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 µm intervals on a Si substrate. We used atomic force microscopy (AFM) to analyze the configuration of AuNWs.

surface-pattering 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.

## Plasma Science and Technology
## Room: 304 - Session PS1-ThA

## Plasma Diagnostics, Sensors, and Control II
**Moderator:** V.M. Donnelly, University of Houston

2:00pm **PS1-ThA1 Spatial Density Distribution of Low-energy Electrons in a 2f-CCP by Laser Absorption and Optical Emission Spectroscopy**, ***T. Ohba***, KEIO University, Japan, *T. Kitajima,* National Defense Academy of Japan, *T. Makabe*, KEIO University, Japan

Optical emission spectroscopy (OES) is widely used as the tool of plasma diagnostics and plasma characteristics. The OES is restricted to the phenomena caused by higher energy electrons over the threshold of the electronic excitation of the target molecule mostly greater than ~10 eV, while the mean energy of electrons in a low-temperature radio frequency plasma is typically 3-5 eV in the bulk plasma, A simple in-situ method to determine spatiotemporally resolved transport of low energy electrons in a two-frequency capacitively coupled plasma (2f-CCP) is presented by using OES and laser absorption spectroscopy in pure Ar.[1] The method employs the long-lived metastable atom Ar($1s_5$) and short-lived excited Ar($2p_9$). Due to the large cross section of metastable atoms with electrons,[2] the net excitation rate of Ar($2p_9$) obtained by OES is expressed as a function of the electron density at the peak energy ~3.3 eV and the metastable density. The spatiotemporal measurement of the electron density distribution with energy of ~3 eV is demonstrated in a typical condition in a 2f-CCP, driven at 100 MHz and biased at 500 kHz in pure Ar at 25, 50 and 100 mTorr. The density shows almost no dependence on time in the bulk plasma and has a sharp peak in the sheath in front of the bias electrode at higher pressure. The influence of photon reabsorption will be further discussed.

[1] M. Ishimaru, T. Ohba, T. Ohmori, T. Yagisawa, T. Kitajima and T. Makabe, Diagnostics for low-energy electrons in a two-frequency capacitively coupled plasma in Ar , Appl. Phys. Lett. 92, 071501 (2008)

[2] A. A. Mityureva and V. V. Smirnov, Opt. Spectrosc. 97, 508 (2004).

2:20pm **PS1-ThA2 Time-Resolved Absorption Spectroscopy with LEDs as Light Source: Application to Etching Plasma Monitoring**, ***G. Cunge***, *D. Vempaire, M. Touzeau, N. Sadeghi*, LTM-CNRS, France

Broad band absorption spectroscopy is widely used to measure the concentration of radicals, which is important to understand the physical chemistry of many plasmas. We show that it is possible to increase significantly the sensitivity of this technique and to perform time-resolved measurement by using Light Emitting Diodes (LEDs) as a light source. This is obtained thanks to the high stability of the LED intensity. By modulating the LED current and using a lock-in amplifier for light detection, it is possible to get rid of the plasma emission, which greatly enhances the reliability of the absorption spectroscopy technique in reactive plasmas. In particular, wavelength dependent absorption cross section can be measured without any distortion, inherent to baseline fluctuations when using other light sources such as Xe arcs. This is particularly important when the species absorbs over a broad band continuum. Finally, we show that it is possible to achieve time resolved measurements of radical density decay in the afterglow of pulsed discharges, giving insight into the gas phase and surface loss processes of these radicals. The method is applied to study radical loss kinetics in BCl3 and SiCl4 based high density plasmas. We concluded that UV absorption with LED is a new and powerful plasma diagnostics, which allows detecting several radicals with a small and low cost equipment, and which may be used for real time process monitoring applications.

2:40pm **PS1-ThA3 Spatio-temporally Resolved Optical Emission Spectroscopy for Investigating rf Plasmas and Micro-Discharges**, ***D. O'Connell***, Queen’s University Belfast, Northern Ireland **INVITED**

Non-thermal low temperature plasmas are widely used for technological applications. Increased demands on plasma technology have resulted in the development of various discharge concepts based on different power coupling mechanisms. Despite this, power dissipation mechanisms in these discharges are not yet fully understood. Of particular interest are low pressure radio-frequency (rf) discharges and also more recently developed micro-discharges at elevated pressure. Optical measurements are a powerful diagnostic tool offering high spatial and temporal resolution. Improved advances in technology and modern diagnostics now allow much better temporal resolution and deeper insight into fundamental mechanisms. In low pressure rf discharges insight into the electron dynamics within the rf cycle can yield vital information. The optical emission from these discharges exhibits temporal variations within the rf cycle, requiring high temporal resolution on a nano-second time scale. These variations are particularly strong, in for example capacitively coupled plasmas (CCPs), but also easily observable in inductively coupled plasmas (ICPs), and can be exploited for insight into power dissipation. Interesting kinetic and non-linear coupling effects are revealed in capacitive systems. In the relatively simple case of an asymmetric rf CCP the complexity of the power dissipation is exposed and various mode transitions (gamma-, alpha-mode and wave-particle interactions) can be clearly observed and investigated. Multi-frequency plasmas, provide additional process control for technological applications. Through investigating the excitation dynamics in such discharges the limitations of functional separation is observed. Recently developed micro-plasmas provide reactive plasma environments for processing applications without the need for expensive vacuum systems. On the one hand they allow extremely localised treatment, e.g. localised surgery. On the other hand they can provide the opportunity for controlled and scalable large area treatment using array devices of thousands or millions of micro-plasmas. However, fundamental understanding of the important mechanisms in particular coupling effects between individual discharge devices is to date poorly understood. Time and space resolved optical emission spectroscopy reveal details of these mechanisms.

4:00pm **PS1-ThA7 A New Diagnostic Based on Fast Atom-Atom Ionization to Measure the Energy Distribution of a Fast Neutral Beam**, ***A. Ranjan***, *V.M. Donnelly, D.J. Economou*, University of Houston

A new diagnostic was developed to measure the energy distribution of a fast (10s to100s eV) neutral beam. Fast neutrals were allowed to collide with slow (thermal) neutrals in a chamber of controlled background pressure (e.g., $10^{-4}$ Torr). A fraction of the fast neutrals was ionized as a result of the atom-atom collisions. The ionized species current was measured as a function of energy with a gridded energy analyzer and off-axis channel electron multiplier, housed in a differentially pumped chamber. The energy distribution of the fast neutral beam was determined from the known cross section of the atom-atom ionization collision as a function of energy. The method was applied to measure the energy distribution of a fast neutral beam formed by surface neutralization of ions, extracted through a grid with high aspect ratio holes (neutralization grid). A pulsed-plasma technique was implemented to achieve an ion beam with a tight energy spread. Ion energy was controlled by a DC bias, applied on an electrode in contact with the plasma, during part of the afterglow period. The electron temperature decays rapidly in the afterglow, which yields a nearly uniform space potential, resulting in an ion beam with tight energy spread. The peak of the NED was ~7% lower than that of the parent ion energy distribution (IED), compared to a ~3% expected energy loss, based on specular reflection. The neutral energy distribution (NED) had a larger energy spread as compared to the parent IED. For example, the FWHM of a NED and the corresponding parent IED were 32 eV and 10 eV, respectively. To study the effect of surface roughness of the neutralization grid, results for a metal grid with a "rough" surface (roughness ~ 10s of nm) will be compared with those of a "smooth" (0.15 nm RMS roughness) silicon grid.

4:20pm **PS1-ThA8 Metastable Probe in Remote Helium Plasma**, ***N. Miura***, *J. Hopwood*, Tufts University

An electrostatic probe for measuring helium metastable density was designed and tested in low-pressure, remote helium plasmas. The measured spatial distribution of helium metastable atoms was then compared with a numerical flow simulation of the plasma. The probe measures secondary electron emission due to helium metastable fluxes at a clean stainless steel surface. The probe consists of a small, planar surface surrounded by an outer guard ring. The outer ring was biased positively to reject plasma ions and the inner part was biased negatively to reject the remaining electrons. In this manner only neutral atoms reach the inner surface, and the inner probe current is due to metastable-induced secondary electrons. Energetic photons generated in the upstream plasma source region were screened from the probe, avoiding photoelectron emission. The experimental gas pressure was 5.5 - 7.5 mTorr inside a 15-cm diameter chamber located downstream from an ICP. Three metastable probes were positioned at different distances downstream from the ICP source and simultaneously swept in the radial direction to obtain spatially-resolved metastable densities. In comparing these measurements to models, the diffusive flow approximation was not completely valid since the mean free path of the metastable atoms was not negligible relative to the chamber dimensions.[1] Therefore, the metastable flow was simulated by both the continuous fluid model and the Monte Carlo method. The results are compared and discussed. The conventional method to measure metastable density is optical absorption, which is well-established and non-invasive.[2,3] That technique gives the density integrated along the optical path and lacks spatial resolution unless Abel inversion is applied. The probe method described here has good spatial resolution, but it is invasive and the secondary electron emission yield is very sensitive to the probe's surface cleanliness.[4] The probe also relies on electrostatic screening due to the biases applied to its surfaces, so the method is only practical in regions of low electron density such as remote plasmas (~$10^8$ $cm^{-3}$).

[1] P.J. Chantry, J. Appl. Phys. 62, 1141 (1987).

[2] A.V. Phelps, Phys. Rev. 99, 1307 (1955).

[3] K.E. Greenberg and G.A. Hebner, J. Appl. Phys. 73, 8126 (1993).

[4] T.A. Delchar, D.A. McLennan, and A.M. Landers, J. Chem. Phys. 50, 1779 (1969).

4:40pm **PS1-ThA9 Etch Process Control with a Deposition-Tolerant Planar Electrostatic Probe**, ***J.P. Booth***, *D. Keil*, *C. Thorgrimsson*, *M. Nagai*, *J. Kim*, *L. Albarade*, Lam Research Corporation

We have implemented the deposition-tolerant ion flux probe described by Braithwaite et al.[1] as an in-situ process monitoring sensor on a commercial dielectric etch tool. The probe head is integrated into the upper (grounded) electrode and is made of the same material, and has been shown to have negligible process impact. With the use of an embedded digital signal processor to analyze the current-voltage characteristics in real-time, this sensor delivers high-precision time-resolved measurements (at 10 Hz) of the ion flux, electron temperature and probe floating potential. In addition, if there are thin films deposited on the probe, the film thickness and conductivity can be determined. This gives unprecedented insight into the power delivery, gas composition and surface state of the reactor during wafer processing. This talk will explore how this information can be used to improve the yield, throughput and cost-of-ownership of production etch tools.

[1] N. St.J. Braithwaite, J.P. Booth, and G. Cunge, Plasma Sources, Science and Technol., 5, 677, (1996).

5:00pm **PS1-ThA10 A New Diagnostic Tool of Radio-Frequency Etching Plasma Produced in Insulated Vessels**, ***H. Shindo***, *K. Kusaba*, Tokai University, Japan

A new method to measure electron temperature and electron energy distribution function by an emissive probe has been proposed.[1] The method is based on measurement of the functional relationship between the floating potential and the heating voltage of emissive probe. From the measured data of the floating potential change as a function of the heating voltage, the electron temperature could be determined by comparing with the theoretical curve obtained under the assumption of Maxwellian distribution. The overall characteristic of the floating potential change could be explained as a function of the heating voltage. The electron temperatures obtained by the present method were consistent with those measured by the rf-compensated Langmuir probe within the error. These experimental verifications were made in the electron density range of $2.6x10^{11}$–$2.8x10^{12}$ $cm^{-3}$ in an inductively coupled plasma of Ar. In this study, a prototype of the diagnostic tool based on the present method was developed in a computer-aided fashion. The method was also applied to a $SF_6$ etching plasma which was produced in ceramic discharge tubes by surface-wave with the frequencies of 13.56 and 60 MHz. In this experiment, the Renium filament was employed, and the erectron energy as well as the potentials were measured in $SF_6$ plasma. These data were found to be consistent with the Si ecth rate obtained in the $SF_6$ plasma. It was stressed that the present method was advantageous in that the probe is operated in a floating condition, hence applicable to plasmas produced in an insulated container. The electron energy distribution function was also obtained in. $SF_6$ etching plasma which was produced in ceramic discharge tubes by surface-wave.

[1] K. Kusaba and H. Shindo, Review of Scientific Instruments, 78,123503(2007).

5:20pm **PS1-ThA11 Near-Real-Time Two-Dimensional Wafer Surface Measurements for Process Optimization and Control**, *C.T. Gabriel*, Spansion, Inc., ***G. Roche***, KLA-Tencor

Optimizing and monitoring plasma etching processes has always relied on one-dimensional data provided by the plasma tool (reflected power, Vdc, optical emission intensity, etc.) or by post-etch measurements such as critical dimensions or film thickness changes. It has long been desired to monitor the plasma condition across the wafer surface in real time. Wafer-level sensors have been developed to measure the temperature of the wafer surface in near real time, and now sensors are being developed to monitor other plasma parameters in a similar way. Here we present measurements of Vrf, a parameter related to the plasma potential, taken from a two-dimensional array of sensors across the surface of a 300 mm wafer processed in a multi-frequency, capacitively coupled industrial plasma for dielectric etching. We show the relationship between Vrf and several process parameters, including RF power, pressure, and CO flow rate. The one-dimensional electrostatic chuck voltage, Vesc, does not respond to these parameters in the same way. Some plasma transients were detected by Vrf that were not detected by Vesc or by optical emission intensity. Vrf appears to correlate with plasma density, and because it is an array of detectors, it proved useful in identifying degraded plasma uniformity at lower CO flows. Such wafer-level Vrf measurements may be valuable for applications such as plasma monitoring, chamber matching, and process optimization to minimize plasma process induced damage.

## Plasma Science and Technology
## Room: 306 - Session PS2-ThA

## Plasma Deposition and Plasma Enhanced Atomic Layer Deposition and Etching

**Moderator:** W.M.M. Kessels, Eindhoven University of Technology, The Netherlands

2:00pm **PS2-ThA1 High Quality Thin Films Deposited at Low Temperatures by Plasma Enhanced ALD and CVD Techniques**, ***C.J. Hodson***, *O. Thomas*, *Q. Fang*, Oxford Instruments, UK **INVITED**

Low temperature deposition of thin films is becoming increasingly important with a growing range of low thermal budget materials being used in device research. The rapid development and predicted future market for plastic electronics has resulted in a greatly increased focus on thin film depositions below 150ºC. This contribution will address the challenges of low temperature deposition in the context of some example applications including; depositing directly onto photo-resist for lift-off, $Si_3N_4$ MIM capacitor technology for MMIC and RF-MEMs[1] and $Al_2O_3$ moisture permeation barriers for polymer based devices such as flexible OLEDs.[2] The study will focus on two chemical vapour deposition (CVD) techniques ideally suited for low temperature deposition namely; Inductively Coupled Plasma CVD and Remote Plasma Atomic Layer Deposition. For any thin film CVD process it is widely true that film quality will degrade at lower temperatures. This degradation is most often measured by decreasing film density, refractive index, breakdown voltage and adhesion; and increasing film impurities and wet etch rates. By using the energetic and reactive plasma species to replace thermal energy it is possible to deposit films with acceptable quality at room temperature, i.e. 25ºC. By generating the plasma remotely such improved film quality can be achieved with low plasma damage to the substrate.

[1] Low temperature high density $Si_3N_4$ MIM capacitor technology for MMMIC and RF-MEMs applications. K. Elgaid, H. Zhou, C. D. W. Wilkinson and I. G. Thayne, Microelectronic Engineering, Volumes 73-74, June 2004, Pages 452-455

[2] Plasma-assisted atomic layer deposition of $Al_2O_3$ moisture permeation barriers on polymers. E. Langereis, M. Creatore, S.B.S. Heil, M.C.M. van de Sanden, and W.M.M. Kessels, Appl. Phys. Lett. 89, 081915 (2006).

2:40pm **PS2-ThA3 An Analysis of the Deposition Mechanisms Involved During Self-limiting Growth of Metal Oxides by Pulsed PECVD**, *M.T. Seman*, CMD Research LLC, *D.N. Richards*, ***C.A. Wolden***, Colorado School of Mines

Self-limiting deposition (~ 1 Å/pulse) of several metal oxides ($Al_2O_3$, $TiO_2$, ZnO, $TiO_2$) has been achieved by pulsed plasma-enhanced chemical vapor deposition (PECVD). In this process a metal precursor and $O_2$ are delivered continuously to a PECVD reactor while the rf power is pulsed at low frequency (~ 1 Hz). With proper reactor design and operation the net deposition rate of pulsed PECVD exceeds that of continuous wave operation, and the quantity of impurities is dramatically attenuated. The growth mechanism of alumina from trimethyl aluminum ($Al(CH_3)_3$, TMA) was investigated by comparing the results from pulsed PECVD with those of plasma-enhanced atomic layer deposition (PE-ALD). For both processes the rate/cycle saturated with ~200 L of TMA exposure. At 165 °C a rate of 1.37 Å/cycle was obtained using PE-ALD. For pulsed PECVD the rate scaled linearly with the TMA partial pressure, and its extrapolation was in good agreement with PE-ALD. The results suggest that deposition in pulsed PECVD involves an ALD component which is supplemented by PECVD growth, and that the contribution of the latter may be tuned using the TMA partial pressure. Experiments using patterned wafers supported this hypothesis. Conformal coatings were observed within 10:1 aspect ratio trenches using pulsed PECVD, however the deposition rate on the surface of these substrates was greater than within the trench. The ratio between the two corresponds well to the ratio of rates obtained from pulsed PECVD and PE-ALD on planar substrates. With cycle times < 1 s, net rates > 30 nm/min were obtained by pulsed PECVD while retaining high quality and digital control.

3:00pm **PS2-ThA4 Self-Limiting Growth of Titania by Pulsed Plasma-Enhanced Chemical Vapor Deposition**, ***N.G. Kubala***, *C.A. Wolden*, Colorado School of Mines

In this presentation we describe the self-limiting deposition (~ Å/pulse) of titanium dioxide by pulsed plasma-enhanced chemical vapor deposition (PECVD) at low temperature (< 150ºC). In this process the titanium tetrachloride (TiCl4) and oxygen are mixed and delivered simultaneously in a remote PECVD configuration. The as-deposited films were characterized by spectroscopic ellipsometry, Fourier transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), and dielectric performance. In addition, the plasma chemistry in this system was characterized using quadrupole mass spectrometry (QMS) and optical emission spectroscopy (OES). QMS measurements confirmed that TiCl4 and O2 are inert in this system in the absence of plasma. During continuous wave plasma operation TiCl4 is completely consumed, no deposition is observed, and the main byproducts are Cl/Cl2. While no film growth is observed with the plasma on or off, self-limiting deposition was readily obtained by pulsing the plasma at low frequency (~1 Hz). The deposition kinetics and film quality were evaluated as a function of precursor exposure, plasma power, substrate temperature, and pulse parameters. The deposition rate per pulse scaled with the degree of precursor exposure during the plasma off step. Through appropriate control of the TiCl4 concentration and pulse duration, the depositing rate may be adjusted over a narrow range (0.6 – 1.3 Å/pulse). High refractive indices were obtained, scaling with exposure and plasma power over a range of 2.3 to 2.6 at 580 nm. The deposition rate also decreased with plasma power, and OES was used to highlight the role of atomic oxygen in this process. XPS analysis showed that the titanium was fully oxidized. At low plasma power a small amount of Cl contamination was observed, however no Cl was detected in films deposited at higher powers. FTIR characterization of these amorphous films display broad absorption features at low wavenumbers that are distinct from the sharp peaks associated with the crystalline phases of TiO2. A comprehensive analysis of dielectric performance is underway and will be reported at the symposium.

3:20pm **PS2-ThA5 Capillary Jet Injection of $SiH_4$ in the HDP-PECVD of $SiO_2$: What We Can Learn from It**, ***R. Botha***, *T. Novikova*, *P. Bulkin*, LPICM, Ecole Polytechnique, France

This paper reports on the deposition of silicon dioxide films from a silane/oxygen gas mixture in a matrix distributed ECR PECVD system. In order to investigate the influence of the primary silane flux and the precursor consumption on the deposition rate and material properties, undiluted silane is first injected into the system through a gas ring positioned around the periphery of the substrate holder, at a distance of 3 cm. The same set of depositions is then done using a 1 mm diameter capillary tube located 3 cm vertically above the substrate surface. The microwave power, pressure, substrate bias and silane gas flow are varied. The material properties are studied using spectroscopic ellipsometry, FTIR spectroscopy and transmission measurements. The plasma is characterized using optical emission spectroscopy (OES) and differentially pumped quadrupole mass spectrometry (QMS). The maximal deposition rate when using a 16 sccm SiH4 and 40 sccm O2 gas mixture is found to increase from 1 nm/s up to 2.16 nm/s when the gas ring is replaced with the capillary jet injection system. This increase is attributed to the large increase in the primary flux of undissociated silane onto the substrate surface. Using an intentionally inhomogeneous deposition resulting from the capillary jet injection and studying the thickness normalized OH absorption in the deposited film at various distances from the capillary injection point, we gain insight into the contribution of the partial pressure of water (which is the main by-product of the reaction between silane and oxygen) on the OH content in the silicon oxide. It is observed that the silicon oxide deposited directly below the capillary injection point has an integrated OH absorption band intensity which is approximately half that of a point 3 cm away from it. Reducing the distance between the injection point and the substrate also leads to a narrowing of the OH absorption band, where the associated vibration mode at 3350 cm-1 practically disappears and only the isolated Si-OH vibration bonds at 3650 cm-1 are retained. By looking at the films thickness at various distances from the capillary jet, it is seen that the primary, beam-like SiH4 is the largest contributor to the deposition rate when using a capillary jet. A Direct Simulation Monte Carlo (DSMC) technique is used to model the flux of the precursor gases onto the substrate plane. The simulation results are compared with the experimental findings.

4:00pm **PS2-ThA7 High Quality TEOS Oxide Film CVD by Microwave RLSA Plasma**, ***H. Ueda***, *Y. Tanaka*, *Y. Ohsawa*, *T. Nozawa*, Tokyo Electron Technology Development Institute, INC., Japan

A high-quality dielectric film CVD in low temperature is required in the processes of nano scale VLSI devices, FPDs, image sensors and flexible organic electronics. There have been many trials to form a high-quality low-temperature silicon dioxide using SiH4-O2 or TEOS-O2 PE-CVD methods. However, they have problems with not only their silicon oxide film qualities but also plasma-induced charging damages to underlying transistors during the plasma process. For example, with regard to the SiH4-O2 PE-CVD, it is hard to exclude Si-H and Si-OH bonds thoroughly to improve electrical properties such as leakage current and dielectric constant. For TEOS-O2 PE-CVD, unreacted TEOS precursor associated with carbon contaminations causes reliability problems and the Si-H and Si-OH contamination was reduced by controlling the plasma source power and Ar gas addition. We report a new low temperature (< 400C) PE-TEOS CVD technology using Microwave (2.45GHz) RLSA (Radial Line Slot Antenna) plasma.[1] It realizes high quality silicon dioxide film without causing charging damages. The film property is as good as a HTO (> 800C) with a good step-coverage performance. The 5%HF wet etch rate of the film is less than that of HTO. One of the unique characteristics of the Microwave RLSA plasma is its plasma generation and transportation system. A very high electron temperature region to produce high density plasma is located just beneath a quartz plate under a microwave antenna. The plasma diffuses to wafer region and the electron temperature in the wafer region becomes less than a half of it in the plasma production region. The electron temperature and density above the wafer in the RLSA plasma chamber can be controlled to produce desired proper precursors for an excellent CVD film by adjusting the pressure, material gas mixture ratio and position of the gas injections. To make the excellent silicon oxide film, the RLSA plasma produces specific precursors with plenty of sufficient oxygen radicals in the gas phase and supplies to the substrate surface. It also seems to provide ions with certain range of energy, that inhibits remaining C=C or C=O bond in the film but enough to proceed surface reaction. In the system, plasma charging damages were never observed even in a MOS capacitor TEG with an antenna-ratio of 1 M, because of the low electron temperature and uniform plasma potential above the wafer surface.

[1] C. Tian, et al.: J. Vac. Sci. Technol. A24 (2006) 1421.

4:20pm **PS2-ThA8 Plasma Polymerization on Textiles: Deposition of Functional Nanostructured Thin Films**, ***S. Guimond***, *Y. Geng*, *A. Ritter*, *B. Hanselmann*, *D. Hegemann*, EMPA, Switzerland

A shift towards highly functional and added-value textiles is now recognized as being essential to the sustainable growth of the textile and clothing industry in developed countries. The demand for tailored surface modifications for water repellence, long-term hydrophilicity, anti-bacterial properties, etc, is therefore increasing. At the same time, the environmental restrictions concerning the waste water produced by conventional textile finishing techniques are getting more and more severe. In this context, plasma processing is seen as an attractive alternative method to add new functionalities to textiles since it is a versatile and eco-friendly (dry) technology. Because plasma processing results in a nano-scaled surface modification, it also has the advantage of preserving the bulk properties as well as the touch of the textiles. In this study, plasma polymer thin films have been deposited on various polyester fabrics of defined structure using $NH_3/C_2H_4/Ar$ low pressure RF glow discharges. The films were first characterized using XPS, FTIR and AFM as a function of the plasma process parameters. For a defined range of energy input and $NH_3/C_2H_4$ gas flow ratio, the coatings are nanostructured and contain predominantly amine functional groups. Interestingly, these films can thus serve as nanostructured templates for further surface functionalization. For example, they can be used to selectively bind acid dyestuff molecules, allowing a very efficient low temperature and substrate independent dyeing. The amine groups contained in the films were also derivatized with molecules containing OH and $CF_3$ groups. Due to the nano roughness and the high specific surface area of the films, super-hydrophilic or -hydrophobic properties are obtained. The hydrophilicity of the various coated fabrics was compared by monitoring the spreading of water droplets with infrared thermography. Results show that the textile structure has an important influence on the final properties. This is discussed in terms of capillary effects and accessibility of the textiles structures to the plasma species. Finally, the properties of the coated fabrics remain generally rather stable during abrasion tests, presumably due to the high crosslinking degree of the films. The scalability of the process investigated in this work has been demonstrated using a pilot-scale continuous web coater.

5:00pm **PS2-ThA10 Tunable Properties of Plasma-Polymerized Organosilicones**, ***V. Cech***, Brno University of Technology, Czech Republic

Plasma-polymerized organosilicones constitute a class of materials with a rich and varied scientific background. This class of materials possesses a special characteristic, which distinguishes it from other plasma polymers – the ability to vary and control the degree of its organic/inorganic character (i.e., the carbon content) by the appropriate choice of fabrication variables. This allows one to control many physicochemical properties over wide ranges resulting in an extraordinary potential for useful applications, which are only now beginning to be tapped. The organosilicon plasma polymers are widely recognized for their potential not only in optical and electronic applications, but also in composites and nanocomposites with controlled interphase. Plasma-enhanced chemical vapor deposition (PECVD) was used to prepare thin films of tetravinylsilane in a mixture with oxygen gas employing an RF (13.56 MHz) helical coupling pulsed-plasma system. Plasma polymer films of the thickness from 0.02 to 1 µm were deposited on silicon substrates at different powers (0.1 – 10 W) and oxygen content (0 – 79%) in mixture. When an appropriate on-time and off-time is selected for pulsed plasma, the physical and chemical properties of hydrogenated amorphous carbon-silicon oxide alloy (a-SiOC:H) may be controlled by the effective power. We will demonstrate that the mechanical properties (Young's modulus 9 – 24 GPa, hardness 0.9 – 4.1 GPa), optical properties (refractive index 1.58 – 1.68 (633 nm), extinction coefficient 0.05 – 0.19 (250 nm), band gap 1.9 – 2.9 eV), and wettability (water contact angle 50 – 83 deg, surface free energy 35 – 58 $mJ/m^2$) of the film may be well tuned in correlation with chemical properties (elemental composition, organic/inorganic character C/Si = 2.5 – 8.6, chemical structure) to prepare tailored materials not only for functional interlayer in polymer composites. The construction of multilayers from individual films of tunable properties will be discussed as well.

5:20pm **PS2-ThA11 Plasma Deposited Films Containing Platinum Nanoclusters as Catalysts for Fuel Cells**, *A. Milella, **E. Dilonardo**, F. Palumbo, R. d'Agostino, F. Fracassi*, Università degli Studi di Bari, Italy

Today, the development of fuel cells is a promising solution to the "energy crisis" and the necessity to provide "clean energy" with virtually zero emission. Fuel cells offer the possibility of abundant energy with negligible emission and high efficiency for converting chemical energy into electricity and heat; however, one of the major disadvantage is their high production cost. Extensive studies are currently addressed to the development of new materials with the aim of improving fuel cell efficiencies and decrease production costs. As far as the catalyst is concerned, nanocomposites films consisting of metal nanoparticles embedded in polymeric matrix are very attractive materials because they allow to decrease the overall amount of Pt while providing high surface area. In literature various approaches have been used to incorporate metal nanoparticles into polymers. In this contribution a one-step plasma deposition process is described to obtain an uniform dispersion of small platinum nanoclusters throughout a thin hydrocarbon matrix. These composite films have been deposited by simultaneous plasma-enhanced chemical vapour deposition (PECVD) of ethylene ($C_2H_4$) and argon (Ar) gas mixtures and RF sputtering of a platinum target. Characterization of platinum-containing plasma-polymerized ethylene films has been realized using X-ray Photoelectron Spectroscopy (XPS), Fourier Transform Infra-Red spectroscopy (FT-IR), UV-Vis spectroscopy, Atomic Force Microscopy (AFM), Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM). Optical Emission Spectroscopy (OES) has been used to correlate the chemical composition of the plasma with the amount of metal embedded in the deposited film. The electrochemical active area of the samples was determined from ex-situ cyclic voltammetry analyses. A comprehensive study on the effect of different plasma parameters (RF power, deposition time, flow rate of gasses) on the chemical composition and structure of the film will be presented. Results show that the platinum content in the coating can be finely controlled by changing the RF power and the monomer flow rate. In particular TEM images confirm that platinum aggregates in crystalline nanoclusters in distributed uniformly in the material. Furthermore the porosity due to the columnar film growth, together with the nanodispersion of the metal clusters, can be advantageously used for catalytic applications.

## 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. Pursel**, 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. Taschuk**, 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 results 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. Taschuk, 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 μL $10^{-4}$ M BPE (trans-1,2-bis (4-pyridyl) ethene) droplet. However, after a layer of ~ 400 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 1μL $10^{-5}$ 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 ($0° < \theta < 90°$). 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 4x4 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 ~450-650 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 ($\Theta_i = 0^0$) and non-normal incidence ($5 \leq \Theta_i \leq 55^0$). 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 ~15 nm to ~30 nm at a vapor incident angle ~75$^o$, 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 ~60 $m^2$/g and ultrathin thickness (~22 nm), which will significantly enhance the kinetics of hydrogen absorption/desorption. The spacing between the nanoblades can also accommodate the large volume change ($Mg \leftrightarrow MgH_2$) 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 ~333 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 ~365 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.

[1] F. Tang, T. Parker, H.-F. Li, G.-C. Wang, and T.-M. Lu, J. of Nanosci. and Nanotechnol. 7, 3239 (2007).

# 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 physiochemical 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.

3:20pm **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 report[1] 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, $H_2{}^{16}O$, $D_2{}^{16}O$ and $H_2{}^{18}O$. By studying the free O-H(D) stretch, present only at the ice surface, all isotopes could be spectroscopically identified. In particularly, 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 $Cu_2O$ and $Al_2O_3$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: Olattic + Vacancies + H2O = 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 $CO_2$ 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. $CO_2$ is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for $CO_2$ 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 $CO_2$ 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 $CO_2$ 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 ($Fe_2O_3$).[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.

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 $\sqrt{3}$x$\sqrt{3}$-R30$^o$ and 2x2 reconstructions of the MgO(111) and NiO(111) surfaces using a combination of x-ray photoelecton spectroscopy (XPS) and transmission electron diffraction (TED). Combined experimental analysis has confirmed that the MgO(111)-$\sqrt{3}$x$\sqrt{3}$-R30$^o$ 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.

## Surface Science
## Room: 208 - Session SS2-ThA

## Novel Reactive Surfaces
## **Moderator:** S. Chiang, University of California Davis

2:00pm **SS2-ThA1 The Photochemistry of Acetaldehyde on $TiO_2$(110)**, ***R.T. Zehr***, *M.A. Henderson*, Pacific Northwest National Laboratory

The ultraviolet (UV) photon induced decomposition of acetaldehyde adsorbed on the oxidized rutile $TiO_2$(110) surface was studied with photon stimulated desorption (PSD) and thermal programmed desorption (TPD). Saturation coverage of acetaldehyde adsorbed on a reduced $TiO_2$(110) surface with 15 % oxygen vacancies exhibited a molecular desorption peak at 235 K along with a higher temperature shoulder at > 260 K that accounts for 1/3rd of the monolayer. Butene desorbing at 530 K was observed as a minor decomposition channel accounting for 1-2% of the adsorbed acetaldehyde. Saturation coverage of acetaldehyde adsorbed on oxidized $TiO_2$ (110) desorbs molecularly at 240 K with a minor decomposition channel (7%) forming adsorbed acetate. Surface bound acetate decomposes to form gas phase ketene in a broad desorption peak centered at 700 K. Acetaldehyde adsorbed on oxidized $TiO_2$ (110) undergoes a facile thermal reaction ($E_a$ = 8 kJ/mol) to form a photoactive acetaldehyde-oxygen complex. Acetaldehyde adsorbed on reduced $TiO_2$ (110) was photo-inactive. UV excitation of substrate charge carriers initiated photofragmentation of the acetaldehyde-oxygen complex resulting in the ejection of methyl radical into gas phase and conversion of the surface bound fragment to formate. The identity of methyl radical was confirmed using isotopically labeled acetaldehyde. The presence of surface bound formate was confirmed by desorption of formate thermal decomposition product, CO, at 550 K. Ejection of reactive organic radical species in $TiO_2$ photoxidation of organics can potentially lead to alternate reaction pathways occurring away from the catalyst surface.

2:20pm **SS2-ThA2 Cesium Promotion in Styrene Epoxidation on Silver Catalysts**, ***L. Zhou***, *R.J. Madix*, Harvard University

The promotion roles of cesium in styrene epoxidation on silver catalysts have been studied by means of temperature-program reaction spectroscopy (TPRS), X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). The TPRS data have shown that the addition of 0.1 ML cesium can inhibit the secondary oxidation of styrene on Ag(111), and more significantly, switch the partial oxidation pathway from the production of phenylacetaldehyde and phenylketene to the production of styrene oxide on Ag(110). The XPS studies have revealed the formation of selective oxametallacycle intermediate and the reduced transformation of this intermediate to a combustion intermediate in the reaction on 0.1 ML cesium-covered silver surface, comparing with the reaction on the clean silver surface. No significant change of the C 1s and O 1s binding energies for certain intermediates was observed, suggesting that cesium does not play obvious electronic effect on the bonding of the intermediates. The STM studies have disclosed an interesting (1x2) reconstruction of the Ag(110) surface induced by cesium and a (3x5) surface oxide structure on the cesium-reconstructed Ag(110) surface. This (3x5)-ordered surface oxide is superimposed on the highly corrugated Ag(111) micro-facets. Our studies provide the insight into the microscopic origins of the structural effects of cesium in styrene epoxidation on silver catalysts.

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[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.

2:40pm **SS2-ThA3 Selectivity and Enantioselectivity on Metal Surfaces**, ***A.J. Gellman***, Carnegie Mellon University **INVITED**

One of the key contributions of surface science to the discipline of catalysis has been the understanding of selectivity in catalytic surface chemistry. The key feature of surface science methodologies that leads to this contribution is the ability to isolate and study elementary chemical reaction steps occurring on single crystal surfaces. These are two independently important attribute of the surface science method. The ability to isolate and then study the kinetics of elementary steps, decouples their kinetics from those of the overall mechanism of which they are part. The use of single crystal surfaces provides homogeneous environments in which the kinetics are not masked by the influence of surface structure. The impact of these aspects of surface chemistry will be illustrated by three examples: study of transition states to elementary catalytic reaction steps, the study of conformational effects in the desorption of large molecules from surfaces and the observations of enantioselectivity in reactions of chiral molecules with chiral surfaces.

3:20pm **SS2-ThA5 Tuning the Reactivity and Selectivity of Chiral Kink Sites on Surfaces through Alloying**, ***A.D. Jewell***, Tufts University, *J.W. Han*, Georgia Tech, *D.O. Bellisario, A.E. Baber, H.L. Tierney*, Tufts University, *D.S. Sholl*, Georgia Tech, *E.C.H. Sykes*, Tufts University

While chiral Cu surfaces have been shown to be enantioselective for certain dehalogenation reactions,[1,2] we seek to develop a surface with a much more general enantiospecific reactivity. To this end, Cu surfaces have been alloyed with a range of more reactive atoms. Simulations of the segregation of different metals to the step edges of Cu(322) has shown that Pd and Ag are promising candidates for segregation to the chiral kink sites of a Cu surface. Depositing reactive atoms selectively at the kink sites will allow us to increase the reactivity while preserving the chiral nature of the kink and thus tune the surface's enantiospecificity. Low-temperature scanning tunneling microscopy has been used to follow the preferred adsorption site of Pd and Ag atoms deposited at step edges on a Cu{111} surface at a variety of temperatures. The Cu{111} is an ideal test bed for this study as it contains large terraces, step edges and equal numbers of R and S kink sites. Alloyed kink sites composed of both Cu and Ag or Pd atoms will have both structural and chemical asymmetry and thus one can expect their enantioselectivity to be enhanced.

[1] Rampulla, D. M.; Gellman, A. J., Surf. Sci. 2006, 600, 2823-2829.

[2] Rampulla, D. M.; Francis, A. J.; Knight, K. S.; Gellman, A. J., J. Phys. Chem. B 2006, 110, 10411-10420.

4:00pm **SS2-ThA7 STM Investigation of the Conversion of Ethylene to Carbon Clusters and Graphite on Pt(111)**, ***A.B. De La Ree***, University of California, Irvine, *V. Johánek*, University of Virginia, *J.C. Hemminger*, University of California, Irvine

New insight has been obtained on the conversion of ethylene to carbon clusters by thermal dehydrogenation on Pt(111). Previous experiments have shown that thermal dehydrogenation following saturation exposure of ethylene to Pt(111) results in the formation of well defined carbon clusters. This occurs through a process of aggregation during the dehydrogenation process in the temperature range from 400K to 700K. Previous experiments have shown that heating an ethylene covered Pt(111) surface to temperatures above 800K leads to the formation of large sheets of monolayer graphite (graphene). The aggregation to form carbon clusters leaves open Pt areas available for additional adsorption. It had not been previously determined whether the adsorption and dehydrogenation of additional ethylene would lead to the growth of the initial clusters or to the nucleation of more clusters of the same size. We have utilized UHV-Variable temperature scanning tunneling microscopy (VT-STM) to address this question. In our experiments, a saturation coverage of ethylene is adsorbed on the Pt(111) surface at room temperature forming a layer of the well known ethylidyne dehydrogenation intermediate. The surface was then heated to 700K leading to further dehydrogenation and formation of carbon clusters that are easily observed by VT-STM. Our STM images show that these carbon clusters are 15±2 Å in diameter and containing an average number of 34±9 carbon atoms per cluster. The surface was then exposed to additional ethylene at room temperature and again heated to 700K. This process was repeated in a number of cycles until the dehydrogenation activity of the Pt(111) surface was completely suppressed. Repeated dosing of ethylene onto the surface followed by annealing led to an increase in the number of carbon clusters without an increase in the size of previously produced clusters. The Pt(111) dehydrogenation activity was completely suppressed after 4 such cycles. The only growth in cluster size that was observed was due to agglomeration of clusters once the surface was covered with a high density of clusters. Continued cycles, such as were utilized in these experiments, leads to the formation of a graphite adlayer on the platinum (presumably via agglomeration of the clusters at high cluster density). This was observed at temperatures well below the onset of long range graphene formation in single ethylene dose experiments.

4:20pm **SS2-ThA8 Catalytic Activity and Morphology of Pt Clusters on the Graphite Surface**, ***T. Kondo***, *K. Watahiki, J.P. Oh, K. Izumi, Y. Iwasaki, D. Sekiba, H. Kudo, J. Nakamura*, University of Tsukuba, Japan

Catalytic activity and surface morphology of Pt vapor-deposited on highly oriented pyrolytic graphite (HOPG) have been investigated by hydrogen-deuterium exchange reaction, scanning tunneling microscopy (STM), temperature programmed desorption (TPD) of CO and in-situ measurement of helium atom scattering (HAS). Based on the STM observation, Pt particles deposited on HOPG with sub-monolayer coverage at room temperature are found to form mostly monolayer clusters on a graphite surface with the reduction in the nearest-neighbor atomic distance of the platinum atoms by as much as 13 % compared to that of the single crystal platinum. Turn over frequency of the hydrogen-deuterium exchange reaction at 24 Torr and 340 K is found to be one order magnitude higher for the monolayer Pt cluster than three-dimensional Pt cluster at 340 K, indicating the smaller adsorption energy of hydrogen on the Pt monolayer cluster. Based on the TPD experiment of CO from Pt/HOPG, the similar catalytic property is found for the monolayer Pt cluster: lower binding energy of CO with Pt compare to the case on the single crystal platinum. These specific catalytic activities are however found to be lost by the slight annealing of Pt/HOPG above 350 K. The change in the catalytic activity is attributed to the change in the morphology of the Pt cluster from monolayer to three-dimensional phase based on the HAS and STM measurements. The higher specific catalytic activity for the Pt monolayer cluster will be discussed in terms of the interface interaction between Pt atoms and the graphite surface.

4:40pm **SS2-ThA9 Surface Structures and Alloy Formation for Ge Deposition on Pt**, *B.E. Koel*, ***G. Liu***, Lehigh University

We have investigated surface structures formed by Ge deposition on Pt(111) and (100) single-crystal substrates by using STM, LEED, ALISS, and XPD. This combination of techniques provides an atomic level description of the surface structures necessary to understand the "site-directed" chemistry of these surfaces and can be used to distinguish formation of adlayers and surface alloys. We find large apparent differences between the behavior of Ge on Pt(100) compared to Pt(111) substrates. An ordered p(√19x√19)R23.4°-Ge/Pt(111) surface alloy was formed on Pt(111) by annealing at 900 K. This structure substitutionally incorporates 4%-ML Ge atoms into the Pt surface layer located very close to substitutional Pt atomic positions, without any corrugation or "buckling". In contrast, and despite extensive bulk solubility of Ge in Pt, it was found that Ge remains on top of the Pt(100) surface as adatoms even after annealing to 1200 K. Furthermore, Pt adatoms produced by lifting of the Pt(100)-hex reconstruction in the vicinity of adsorbed Ge do not intermix with the Ge but rather segregate to form pure-Pt islands with Ge adsorbed on top. We interpret the c(2x2) Ge overlayer that is produced by 0.5 ML Ge deposition and annealing at 600 K as formation of a unique surface alloy or "layer compound". The Pt(100) substrate thus is covered by a surface alloy film with the structure of a body-centered tetragonal $Pt_2Ge$ layer compound. TPD shows that both CO and NO adsorb more weakly on the Pt-Ge bimetallic surfaces than on the clean Pt surfaces.

5:00pm **SS2-ThA10 Revisiting the Oxidation Kinetics of Plutonium Surfaces**, ***H.G. García Flores***, University of Nebraska-Lincoln and Los Alamos National Laboratory, *D.P. Moore, J.P. Baiardo, D.L. Pugmire*, Los Alamos National Laboratory

The oxidation of metal surfaces is an important application of kinetic modeling because it allows for the study of the influence of transport processes in a gas-solid reaction. Understanding the oxidation kinetics of plutonium is desired because this process can have an impact in the storage and handling of this radioactive element. The goal of this presentation is to investigate the early stages of the corrosion of plutonium in an attempt to elucidate the oxidation kinetics, in particular at the initial rapid stage of the oxidation. The data presented here will be evaluated with an inverse-logarithmic kinetic rate law, which has not previously been used to describe the oxidation kinetics of plutonium. The paralinear and parabolic models generally employed to describe oxide film growth of plutonium do not explain this rapid initial stage of oxide film growth of plutonium. To this aim, ellipsometry, x-ray photoelectron spectroscopy (XPS) & Auger electron spectroscopy (AES) data recently collected at Los Alamos and the ellipsometry data presented by Larson & Cash in the Journal of Physical Chemistry[1] will be used to perform a comparison of the kinetic models for oxygen corrosion of plutonium.

[1] D.T. Larson, D.L. Cash, J. Phys. Chem., 73 (1969) 2814.

5:20pm **SS2-ThA11 Kinetics of Hydride Front in Zircaloy 2 and H Release from a Fractional Hydrided Surface**, *M. Diaz,* Instituto de Ciencia de Materiales de Madrid, Spanish National Research Council, Spain, *B. Remartinez, S. Perez,* Iberdrola, S. A., Spain, ***J.L. Sacedon***, Instituto de Ciencia de Materiales de Madrid, Spanish National Research Council

In these Zirconium based materials, when the $H_2$ dissociation at a surface is enough efficient, a continuous and compact hydride layer is formed, increasing in thickness with time. Using a UHV equipment and method, specifically developed to compare the resistance to hydriding of tubular nuclear fuel claddings,[1] the propagation kinetics of the Hydride/metal interface through the cladding thickness is obtained. It results in a hydride thickness vs time dependence th =K $t^a$, where a is close to 1/2 and a rate dependence on the thickness dth /dt =C $th^b$ where b is close to -1. They are near to the expected values from an H ideal diffusion through the Hydride layer, and differ from the linear kinetics (a =1) and other fractional a exponents obtained from thermo-gravimetric methods. At difference, in our method the sample is directly heated in an UHV environment, which allows a fast control of the local temperature where the hydriding reaction takes place. At the same time, pure $H_2$flows inside the tube, starting the hydriding from the inner tube surface. The method allows determining the formation enthalpy of $ZrH_{1.5}$ (Zircaloy2) H=-117±8 kJ/mol at 295.5 K, giving the second determination of this value in the literature.[2] Being the Hydride composition determinate by X ray diffraction methods, mass spectrometry allows to follow the $H_2$ desorption produced by the surface reaction $H_s+H_s = H_2$[3] at the external surface of the tube, opposite to surface where the hydriding begins. A kinetic model and expression that explain the $H_2$ desorption curves is presented. In this model the H desorption rate, is proportional to a fractional surface Hydride coverage. This coverage increase in time by the excess of H precipitated from the H oversaturated metal. The Hydride/ metal interface acts as a very weak H source feeding the metal over saturation. The ratio between the of H flux precipitated at the external metal surface to that precipitated at the Hydride / metal interface is determinate to be $\leq 10^{-6}$.

[1] J. L. Sacedón, M. Díaz, J.S. Moya, B. Remartínez and J. Izquierdo, Journal of Nuclear Materials. 327 (2004) 11.

[2] P. Dantzer, W.L., T. B. Flanagan and J. D. Clewley, Metall. Transact. A. 24 (1993) 1471.

[3] D. E. Sheleifman, D. Shaltiel and I. T. Steinberger, J. Alloys and Compounds. 223 1995) 81.

## Thin Film
## Room: 302 - Session TF-ThA

## Thin Films for Displays and Flexible Electronics
**Moderator:** J. Grace, Kodak

2:00pm **TF-ThA1 Thin Film Challenges for Flexible Displays and Electronics**, ***R. Ma***, *M. Hack, J. Brown*, Universal Display Corporation **INVITED**

In this paper, after a brief review of the history and current status of flexible displays and electronics, we will discuss in detail the development of one of the most challenging devices, a flexible full color active matrix organic light emitting diode (OLED) display. We will focus in the three areas: ultra-thin flexible TFT backplanes, rugged thin film barrier protection, and the flexibility of the overall system. The use of flexible substrates generates two main challenges: the handling of the flexible substrates and the compatibility of TFT process to substrate property. Both semiconductor and TFT-LCD industries are built on rigid substrates so the traditional process can't be applied directly to flexible substrates. Mis-match of thermal properties between substrates and TFT materials/process will result failed backplanes. We have chosen thin metal foils as the substrates for flexible displays because of their excellent thermal, mechanical and permeation barrier properties and good flexibility. Metal foils as thin as 25 mm have been used and planarization process has been developed. Another key challenge is to develop a flexible thin film permeation barrier. OLEDs degrade as a result of exposure to atmospheric oxygen and water. Working with Professor Wagner's team at Princeton University, we have identified a flexible, highly impermeable barrier layer that is deposited from environmentally-friendly and inexpensive precursors in a single-chamber reactor. The lifetime of OLEDs encapsulated with the layers exceeds the industrial target of 1,000 hours and also the lifetime of conventionally sealed glass packaged OLEDs. Many materials are used in a flexible AMOLED: organic, inorganic and metallic systems. We have studied the characteristics of such materials and developed an initial system to study the mechanical flexibility of the integrated device. We will present the required material building block properties and present recent results on ultra-thin (< 50 µm) flexible OLED displays. Flexibility results on these displays show that they operate when conformed to a tight diameter of only 5 mm.

2:40pm **TF-ThA3 Roll-to-Roll Plasma Enhanced Chemical Vapor Deposition of Graded Ultra-high Barrier Coatings on Polymer Substrates**, ***M. Yan***, *R.A. Zhao, D.J. Smith, C.L. Jones, P.A. Mcconnelee, A.G. Erlat, A.R. Duggal, T.P. Feist*, GE Global Research

The use of plastic film substrates for organic electronic devices promises to enable new applications, such as flexible displays and conformal lighting, at low cost through high volume roll-to-roll fabrication. Unfortunately, presently available substrates cannot yet deliver this promise because of the challenge in achieving the required combination of optical transparency, impermeability to water and oxygen, mechanical flexibility, and high temperature capability. In this contribution, we describe our roll-to-roll (R2R) plasma enhanced chemical vapor deposition (PECVD) process development and performance of a unique graded transparent ultra-high gas barrier coating on top of plastic substrate which is aimed at meeting this challenge.

3:00pm **TF-ThA4 Latest Innovations in Large Area Web Coating Technology via PECVD Source Technology**, *M.A. George, J.E. Madocks, J. Morris,* ***H. Chandra***, General Plasma

In this paper we discuss the latest results of our development of large area PECVD source technologies for flexible substrates. A significant challenge for flexible displays is the economical application of thin films for use as vapor barriers, transparent conductive oxides, optical interference thin films and thin film silicon. Here at General Plasma we have developed two innovative PECVD source technologies that provide an economical alternative to low temperature sputtering technologies and enable some thin film materials not accessible by sputtering. The Penning Discharge Plasma (PDP™) source is designed for high rate PECVD depositions on insulating temperature sensitive web.[1] This technology has been utilized to deposit SiO2 and SiC:H for barrier applications.[2] The Plasma Beam Source (PBS™) is useful for deposition on conductive or rigid substrates or for deposition of thin films that are sensitive to the high ion bombardment flux inherent to the PDP technology. We have developed thin film processes in our laboratory for deposition of SiO2, SiC:O, SiN:C, SiN:H and thin film silicon via this PBS source.[3] We discuss the patented source design, plasma physics and chemistry of the deposited thin films.

[1] J.Madocks; "High Rate PECVD Source for Flexible Substrates", Proceedings of the Society of Vacuum Coaters, pp 187, 2003.

[2] V. Shamamian, L. Zambov, U. Pernisz, S. Kim, S. Perz and G. Cerny, "Progress in the Development of SiC:H Alloy Film on Flexible Substrates for Extremely Low Moisture Permeability Applications", Proceeding of the Flexible Displays and Manufacturing Conference, 2006.

[3] M.A. George, P. Morse, J. Morris, H. Chandra and J. Madocks, "Deposition of Silicon Oxide, Silicon Nitride and Silicon Carbide Thin Films by New Plasma Enhanced Chemical Vapor Deposition Source Technology", Conference Proceedings of the Assoication of Industrial Metallizers, Coaters and Laminators (AIMCAL), 2007.

3:20pm **TF-ThA5 Low Damage Sputter-Deposition System for the Deposition of TCO Films on Organic Films**, *H. Lei, K. Ichikawa, T. Uchida,* ***Y. Hoshi***, Tokyo Polytechnic University, Japan

We examined damages produced in organic materials during sputter-deposition of electrode film by measuring a change of photo-luminescence (PL) intensity of organic light emitting materials and developed a low damage sputter-deposition system. MEH-PPV as polymer and BAlq3 as small molecule were used for the light emitting materials. We compared the damages produced in the deposition of electrode films(ITO) by using different types of sputtering systems, i.e., a facing target sputtering (FTS) system and a conventional planar rf-magnetron sputtering (rf-MS) system. By using FTS system, decrease in PL intensity was suppressed remarkably compared with the using of rf-MS. In addition, removing the bombardment of high energy secondary electrons to the film surface was very effective to reduce the damages of the organic films. Furthermore, reduction of kinetic energy of deposition particles to the organic film surface by increasing sputtering gas pressure was necessary to reduce the damages of the organic films. Finally, we could deposit ITO films on the organic films without damages by using a FTS system, where bombardment of high energy negative oxygen ions, high energy secondary electrons, and high energy deposition particles to the organic film were completely removed.

4:00pm **TF-ThA7 Sputter Deposition of Highly Flexible ITO on Polymeric Substrates**, *M. Yan, A.G. Erlat,* ***B. Scherer***, *P.A. Mcconnelee, A.R. Duggal, T.P. Feist*, GE Global Research

This contribution describes a novel modification to conventional DC magnetron sputtering setup to make highly flexible, conductive and transparent indium tin oxide (ITO) coatings on polymeric films. Such high quality ITO coated polymeric film serves as an ideal substrate for flexible optoelectronic devices such as organic light emitting diodes (OLED), photovoltaics, organic electrochromic devices, and the like. The uniformity and flexibility of ITO coatings on plastic substrates were dramatically improved by inserting a shadow mask between substrate and ITO sputter target and critically positioning the mask to block a spatial region of the sputtering target material from depositing on the substrateIn addition, ITO sputtering process repeatability was improved by preconditioning sputter chamber after cleaning.

4:20pm **TF-ThA8 Thermally Stable Very Thin Ag Films for Electrodes**, ***M. Kawamura***, *D. Fukuda, Y. Inami, Y. Abe, K. Sasaki*, Kitami Institute of Technology, Japan

Low resistivity metals such as Cu or Ag have been paid attention for substituting Al alloy films as gate, source, and drain electrodes in LCD-TFT. Though Ag features with the lowest resistivity among all metals, some serious demerits, e.g. agglomeration by heating, are known. Improvements of thermal stability of Ag thin films have been attempted by especially alloying the Ag films, but it is difficult to preserve its low resistivity due to impurity scattering effect in some cases. We have showed a result of structural modification, where very thin Al oxide layer (about 3 nm of thickness) were introduced at top and bottom of the Ag films (about 95 nm), namely Al/Ag/Al structure. This structure showed excellent stability on surface morphology and electrical resistivity even after annealing at 600ºC in vacuum. The resistivity of the film was also as low as that of bulk Ag. Next, reduction of Ag layer thickness down to 50 nm was attempted. The resistivity and morphology of the film were degraded slightly but remarkably superior to those of pure Ag films, and also those of Cu thin films with the same size. Consequently, it is found that the modified Ag films show excellent electrical properties and can be used at elevated temperatures.

4:40pm **TF-ThA9 High Rate Sputtering Deposition of Silicon Oxide Thin Films from New $SiO_2$:Si Target Composition**, ***Q.H. Fan***, Wintek Electro-Optics Corp, *L.Q. Zhou*, University of Michigan, *D. Stevenson*, Wintek Electro-Optics Corp.

Silicon oxide thin films are widely used in flat panel displays as well as optical and large area architectural type coatings. Two sputtering techniques are commonly used to deposit silicon oxide thin films. For the highest density $SiO_2$ films RF sputtering using quartz targets is normally preferred. For large area coating at high rates reactive sputtering using silicon targets and either DC or AC type power supplies is the most common method. RF sputtering results in high quality films but relatively low deposition rates. Reactive sputtering from silicon targets has higher deposition rates but lower film quality. In addition reactive sputtering using planar targets has process stability issues due to target poisoning. The ideal process would combine the high rates of reactive sputtering with the film quality of RF sputtered $SiO_2$ films from quartz targets. We have successfully developed a conductive $SiO_2$:Si target (patent pending) that achieves this goal. This target composition can be sputtered using DC, AC or RF power supplies. Using this new target it is possible to reach deposition rates that are at least three times higher than typical RF sputtered $SiO_2$ films from quartz targets. Further, the $SiO_2$ film quality that can be achieved is comparable to RF sputtered films from quartz targets. In this paper, we present details of the conductive $SiO_2$:Si target as well as the resulting $SiO_2$ film properties and deposition rates that have been achieved. In addition we also provide our preliminary analysis of the deposition process mechanism that enables such high deposition rates and film quality when $SiO_2$:Si targets are used.

5:00pm **TF-ThA10 Recent Development of Low Temperature Plasma Enhanced CVD of Transparent Conducting Oxide in Photovoltaic Applications**, ***H. Chandra***, *M.A. George, S. Higgins, P.L. Morse, J.E. Madocks*, General Plasma Incorporated

Transparent conducting oxide (TCO) is a key component for photovoltaic and display applications. Indium tin oxide (ITO) is the best known TCO material with regard to electrical and optical properties. However, ITO is prohibitively expensive for economical production for these applications. One candidate to replace ITO as TCO material is fluorine-doped tin oxide. It is stable at high temperature, economical to produce and less reactive compared to other TCO materials such as zinc-oxide based TCO[1]. The bulk resistivity of tin oxide films deposited with conventional method (PECVD, spray pyrolysis, atmospheric pressure CVD) is as low as $2x10^{-4}$ Ohm-cm.[1] However, the deposition temperature is typically above 350°C which has limited use for temperature sensitive processes such as quantum dots based solar cells or large area plastic substrates. We have developed a novel PECVD system to deposit tin oxide at lower temperature (below 200°C) while achieving good conductivity. Our tin oxide films have bulk resistivity below $4x10^{-3}$ Ohm-cm at 200°C which is lower than conventionally deposited films at the same process temperature. Furthermore, the linear PECVD source used in this process is scalable to several meter-wide web substrates with film uniformity better than 3%. The deposition rate is typically 200-400 nm-meter/minutes more than an order of magnitude higher than competing sputtering technologies. The scalability to large area with excellent uniformity coupled with high deposition rate is important for economical production of TCO layer. In the present work, we will discuss the PECVD source used in the process, electrical properties (carrier concentration and mobility), optical properties and microstructure of the deposited tin oxide and other TCO thin film materials.

[1] W. Beyer et al., "Transparent conducting oxide films for thin films silicon photovoltaics," Thin Solid Films 516, 147 (2007).

5:20pm **TF-ThA11 Field-Effect Mobility Enhancement of Organic Thin Film Transistors on Flexible Substrates with Organosilanes-based Surface Modification**, *C.G. Takoudis*, ***L. Jiang***, University of Illinois at Chicago, *J. Zhang, D.R. Gamota*, Motorola

In Organic Thin Film Transistors (OTFTs), the performance is profoundly affected by organic semiconductor crystal formation or organic structure ordering. As it is known, the ability of conjugated molecules to transport charge due to the π-orbital overlap of neighboring molecules provides their semiconducting and conducting properties. The self-assembling or ordering of these molecules enhances this π-orbital overlap and is the key to improvements in carrier mobility. Since the semiconductor materials are deposited on dielectric layer, the surface chemical and mechanical properties of dielectric materials do affect the alignment and the crystal formation of semiconductor. For industrial applications requiring large area coverage, structural flexibility, and low cost, such as printed electronics, each layer is printed on the flexible plastic substrate, so that the dielectric materials have to be printable. In this work, poly(4-vinyl phenol-co-methyl methacrylate) (PVP-PMMA) was used as dielectric cross-linked at 200ºC by mixing with p- Tolyltrimethoxysilane (TTMS) on polyimide substrate, and Aluminum deposited on the polyimide as gate. The carbon ink could be printed on the cross-linked PVP-PMMA to form source and drain. Solution processed bis(triisopropylsilylethynyl) (TIPS) pentacene was deposited either by drop casting or rod coating and the field effect carrier mobility of $10^{-3}$ ~$10^{-5}$ $cm^2/V•s$ were obtained. The resulting structures and systems were also characterized with differential scanning calorimetry and atomic force microscopy.

## Biomaterial Interfaces
## Room: Hall D - Session BI-ThP

## Biomaterial Interfaces Poster Session with Focus on Engineered Bio-Interfaces and Sensors

**BI-ThP2 High-Sensitivity Surface Enhanced Raman Scattering of Sub-Picomole Level of Adenine and Thymine Species at Au/Ag Nanoparticle Modified Silicon Nanotip Arrays,** ***H.C. Lo,*** National Chiao-Tung University, Taiwan, *H.I. Hsiung,* National Taiwan University, *Sv Chattopadhyay,* National Yang-Ming University, Taiwan, *C.F. Chen,* Ming-Dao University, Taiwan, *J. Leu,* National Chiao-Tung University, Taiwan, *K.H. Chen,* Academia Sinica, Taiwan, *L.C. Chen*, National Taiwan University

Optical sensing of adenine and thymine nucleic acid species have been achieved at the femtomolar level using self assembled gold and silver nanoparticles coated silicon nanotips (SiNTs) arrays. The use of sub-10 nm metal particulates with optimum density and inter-particle distance ensures such high levels of sensitivity in surface enhanced Raman scattering experiments. In this work wafer-scale silicon nanotip arrays were fabricated using a patented self masked dry etching technique to provide an excellent platform for the metal self assembly. This structure consists of the SiNTs with apex and bottom diameter of ~ 1 nm and ~ 100 nm, respectively, length of ~ 1000 nm and density of $10^{11}/cm^2$. The high density of gold and silver nanoparticles and short inter-particle distance enabled the bio-immobilization and amplification of the Raman signals of adsorbed molecules, allowing identification of minute amount of the adsorbed molecules with chemical specificity. The high sensitivity of surface enhanced Raman scattering can be maintained over a considerable period of time. The vibrational Raman signals of immobilized species can be detected even after four months of conservation. The straightforward, binder-less, stable and room temperature bio-molecular detection underlines the effectiveness of surface enhanced Raman scattering vis-á-vis fluorescence.

**BI-ThP3 Characterization of Functionalized Layers on Silica Surfaces for DNA Attachment,** ***R.A. Shircliff,*** *J.F. Fennell,* Colorado School of Mines, *I.T. Martin, P. Stradins,* National Renewable Energy Laboratory, *S.G. Boyes,* Colorado School of Mines, *M.L. Ghirardi,* National Renewable Energy Laboratory, *S.W. Cowley,* Colorado School of Mines, *H.M. Branz*, National Renewable Energy Laboratory

The morphology and chemistry of functionalized silica surfaces have been characterized to understand key factors to surface uniformity and reproducibility of DNA immobilization and hybridization. Deposited 3-aminopropyltriethoxysilane (APTES) and 3-aminopropyldimethylethoxysilane (APDMES) layers were characterized by x-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), spectroscopic ellipsometry, thermogravimetric analysis, contact angle and DNA bioassays. DNA bioassays included fluorescence-based analysis and $^{32}$P-radiometric assays of DNA surface density. Angle-resolved XPS confirmed attachment of the sulfo-EMCS heterobifunctional crosslinker to amine-terminated layers deposited from both APTES and APDMES. High levels of immobilization of thiolated single-strand DNA to APTES-modified surfaces were observed by fluorescence from fluorescein dye attached to the DNA. Surprisingly, there was no detectable attachment of thiolated DNA to surfaces modified with monolayer films from APDMES. AFM of the APTES film revealed up to micron-scale island formations, which were likely caused by polymerization in the solution phase or on the surface. The APTES films also had significant variations of morphology under nominally identical deposition conditions, which may correlate with irreproducibility in DNA attachment. In contrast, the APDMES films had sub-nanometer surface roughness. Deposition of APTES, commonly used in DNA microarrays, showed high immobilization efficiency but lacked good reproducibility. APDMES films, which can only form a monolayer, showed reproducible monolayer films but lacked measurable DNA attachment. As an alternative to silane films, preliminary results will be reported on poly(ethylene glycol)-based films in order to improve reproducibility of DNA immobilization. We gratefully acknowledge the NREL Laboratory Directed Research and Development program for project funding. One of us (JFF) was supported by the U.S. Army.

**BI-ThP4 PNA-PEG Modified Silicon Platforms as Functional Bio-Interfaces for Applications in DNA Microarrays and Biosensors,** ***A. Cattani-Scholz,*** *D. Pedone, F. Blobner, G. Abstreiter,* Technical University Munich, Germany, *J. Schwartz,* Princeton University, *M. Tornow,* Technical University Braunschweig, Germany, *L. Andruzzi*, Ludwig-Maximilians University Munich, Germany

Bio-functional interfaces on semiconductor materials enjoy increasing interest in basic and applied sciences because of the many possible applications of these structures in, e.g., proteomics, micro-array technology and biosensors. For DNA sensing applications single stranded DNA or peptide nucleic acid (PNA) is commonly covalently immobilized via a linker onto the surface which has been pre-modified with a thin organic film before. Here, high hybridization efficiency is generally strived for, together with a maximum suppression of unwanted, nonspecific interactions between target DNA and the sensor surface. We report on the synthesis and characterization of two novel types of PNA interfaces on silicon/siliconoxide substrates featuring poly(ethyleneglycol) $(PEG)_n$ as molecular spacer and backfilling. As type one, phosphonate self-assembled monolayers were derivatized with a 12mer PNA oligomer via modification with and post-functionalization of a maleimide-terminated poly(ethyleneglycol) spacer ($PEG_{45}$). Similarly, a type two modification consisted of silane self-assembled monolayers which were functionalized with PNA via modification with a maleimide-terminated $PEG_{45}$ spacer and were also subsequently modified with a shorter methoxy-terminated $PEG_{12}$ (back-filling). X-ray photoelectron spectroscopy (XPS) analysis confirmed binding of PEG and PNA to the phosphonate and silane films and indicated that additional PEG chains were tethered to the surface during the backfilling process. We carried out hybridization experiments in the presence of matching and mismatching, fluorescently labeled DNA and found that both types of bio-functional surfaces were effective in the hybridization of matching DNA while significantly reducing non-specific adsorption. To verify the suppression of DNA adsorption on PEG-only modified surfaces and to extend the scheme towards laterally patterned structures we employed micro-molding techniques, i.e., pressed DNA-coated PDMS stamps onto a surface which comprised of alternating PNA functionalized, and non-functionalized regions, respectively, in a grid-like manner. These studies confirmed that hybridization took place selectively at the PNA functionalized regions only, while physisorption at the probe-less PEG-functionalized regions was drastically reduced.

**BI-ThP5 Lipid Bilayer Formation and Properties Studied by Combined Electrical Impedance Spectroscopy and QCM-D,** ***E. Briand***, *F. Höök, B. Kasemo, S. Petronis*, Chalmers University of Technology, Sweden

The added value of using synchronized Electrochemical Impedance Spectroscopy (EIS) and Quartz Crystal Microbalance with Dissipation (QCM-D) monitoring is that phenomena and properties, hidden for one of the techniques, may be dynamically resolved by the other one. EIS provides information about the electrical properties of the studied system, while QCM-D provides information about adsorbed mass variations and viscoelastic properties of the adlayer. We have here applied these combined techniques to study (i) supported lipid bilayer formation and (ii) subsequent pore formation using gramicidin D. The results demonstrate how these techniques in combination provide new insights about this and similar bio-adlayer systems. (i) The signatures, produced by the two techniques, of lipid bilayer formation on SiO2 from nanosized POPC liposomes, are quite different. The well established QCM-D signature tells that the initial kinetic phase consists of intact liposome adsorption, followed by vesicle rupture and fusion of lipid bilayer patches to a coherent bilayer. In contrast, EIS does not show any change in impedance until slightly before the critical liposome coverage is reached, where rupture and bilayer formation begins. Furthermore, at the end of the process, where the QCM-D $\Delta f$ and $\Delta D$ signals have reached stable bilayer values, the electrical resistance still varies for several minutes, indicating a rearrangement/annealing process and/or additional minor addition of lipids. The absolute value of the bilayer resistance was found to significantly improve when cations were present in the buffer. (ii) Using a high resistance bilayer as the starting point, the insertion of gramicidin D was followed by QCM-D and EIS. By simultaneously recording EIS signals and changes in the viscoelastic properties (QCM-D) of the bilayer, at different GrD concentrations it was possible to identify the range of concentrations suitable for combined studies of the peptide activity and pore formation.

**BI-ThP6 A Simple Method for Making Highly Ordered Chemical Patterns by Sputtering Through Ordered Binary Colloidal Crystals**, *G. Singh, V. Gohri, S. Pillai, A. Arpanaei, M. Foss, **P. Kingshott***, The University of Aarhus, Denmark

Nanopatterning of biomolecules, such proteins, DNA, and polysaccharides are of great interest in cell culture dishes, biosensors, medical implants and tissue engineering. These so-called nanoarrays require attachment of biomolecules at specific locations on solid substrates with precisely controlled chemistry, but to function fully the non-specific adsorption in surrounding regions must be prevented. Currently, the most widely used techniques for patterning are photolithography, soft lithography, or dip-pen AFM lithography, all of which involve multi-step surface modification directly onto substrates, and are time consuming and expensive. We have shown recently that highly ordered binary polystyrene nanoparticle patterns can be generated from simple self-assembly onto surfaces, where single layers of large particles are surrounded by crystals of smaller particles. Here, we report a novel method for generating chemical nanopatterns by Au sputtering through the crystal layer followed by lift-off of the particles. The crystal regions of the binary pattern, composed of the smaller particles, facilitate transport of the Au sputter beam to the substrate. After particle lift-off only the regions where the small particles have been in contact with the silicon substrate are coated with Au. The large particles act as a mask and remain uncoated, and the thickness of the surrounding Au layer is controlled by the sputter time. The highly ordered chemical patterns are generated where the size of the features are tuned by appropriate choice of particle sizes (50nm to 3µm diameters) and ratios. The stability of the Au layers to aqueous environments is ensured by coating the Si wafer with a thiolated silane, which acts as an adhesion layer. We demonstrate that the resultant Au layer can be coated with a protein resistant mercapto-oligo(ethylene glycol) layer ((1-mercapto-11-undecyl)-tri(ethylene glycol)) that allows selective adsorption of fluorescently labelled proteins on to the Si regions of the pattern. The Au patterns and subsequent protein adsorption are characterized by AFM, SEM and fluorescent microscopy. XPS and ToF-SIMS are used to characterise the chemical modification steps of the patterning. In summary, we introduce a novel method for generating highly-ordered chemical nanopatterns that is very fast, inexpensive, and allows patterns of biomolecules to be created over large areas.

**BI-ThP7 Smooth $SiO_2$ Surface for Biointerfaces Applications Obtained by Oxidation of Polysiloxane Thin Films**, ***C. Satriano**, G.M.L. Messina,* University of Catania, Italy, *S. Svedhem,* Chalmers University of Technology, Sweden, *G. Marletta,* University of Catania, Italy, *B. Kasemo*, Chalmers University of Technology, Sweden

A simple approach for preparation of smooth $SiO_2$ surfaces by oxidative modification of polysiloxane films is described. Thin films of poly(hydroxymethylsiloxane) (PHMS) were deposited by spin coating on silicon or gold substrates and modified either by radiofrequency oxygen plasmas or combined oxygen plasmas and thermal treatments. The modified films were converted to $SiO_x$ phases, ultimately $SiO_2$ like, as determined by XPS, and exhibited very high water wettability, as measured by contact angle measurements. Moreover, the high original flatness of the PHMS was not affected by the modification treatments. Both untreated and treated films had roughness values below one nanometer. Using the QCM-D and SPR techniques the adsorption behaviour of and supported lipid membrane (SLB) formation, from small unilamellar vesicles of neutral zwitterionic POPC, positively charged DOEPC and negatively charged DOPC/DOPS mixtures were investigated onto untreated and modified PHMS films. SLBs were successfully obtained on the modified PHMS surfaces. The latter results are compared with corresponding results for PVD deposited $SiO_2$.

**BI-ThP8 Influence of Raft Forming Lipids on Bilayer Formation on $SiO_2$ Surfaces Studied by Means of QCM-D**, ***M. Sundh**,* University of Aarhus, Denmark, *S. Svedhem, B. Kasemo,* Chalmers University of Technology, Sweden, *D. Sutherland*, University of Aarhus, Denmark

It is well known that artificial bilayers composed of ternary lipid mixtures of phosphatidylcholine, sphingomyelin (SM), and cholesterol (chol) phase separate and form domains enriched in SM and chol; so called rafts. Rafts are believed to be involved in numerous cellular processes such as cell signaling, endocytosis etc.[1] and thus the importance of their study. Developments in the field of nanotechnology have opened up new routes to the study of molecular systems. The long term goal of these studies involves the use of nanostructured interfaces to systematically define parameters such as membrane curvature and allow the investigation of their correlation to phase separation. As a preliminary step the formation and quality of bilayers, formed with lipid raft compositions, on flat surfaces is investigated. Quartz crystal microbalance with dissipation (QCM-D) is a tool commonly used to study and quantify the adsorption of proteins and the fusion of lipid vesicles into lipid bilayers.[2] In this study the influence of lipid composition in lipid vesicles on the formation of bilayers was investigated and interpreted in terms of the phase separation of the components. Ternary lipid mixtures of POPC/SM/chol at different ratios were formed into unilamellar vesicles by extrusion and deposited on $SiO_2$ coated QCM crystals. Preliminary results show that the formation of lipid bilayers can be tuned by changing the lipid composition or temperature. An increase in the proportion of SM within the vesicles results in a reduction in quality of the formed bilayer, seen by an increased dissipation response. These results can be interpreted in terms of phase separation into ordered and disordered fluid domains within the vesicles. As the SM concentration is increased the ordered phase becomes dominant up to a point where the vesicles are too rigid to fuse and form bilayers. A temperature study of vesicles with POPC/chol shows that rupture of vesicles could be induced by doing the experiment at increased temperatures and hence changing the lipid phase.

[1] Simons, K. and D. Toomre, Lipid rafts and signal transduction. Nat Rev Mol Cell Biol, 2000. 1(1): p. 31-39.

[2] Reimhult, E., F. Hook, and B. Kasemo, Intact vesicle adsorption and supported biomembrane formation from vesicles in solution: Influence of surface chemistry, vesicle size, temperature, and osmotic pressure. Langmuir, 2003. 19(5): p. 1681-1691.

**BI-ThP9 Investigation and Reduction of Current Noise in Solid-State Nanopores**, ***D. Pedone**, M. Firnkes, G. Abstreiter, U. Rant*, Technical University Munich, Germany

Solid state nanopores have emerged as powerful analytical tools to study single molecules. DNA translocation experiments have been conducted with great success in the past, and protein translocation has been demonstrated recently. In these experiments, the biomolecule is detected by measuring the ionic current through the pore, which becomes transiently suppressed when a molecule traverses the pore. The use of solid-state nanopores for studies of complex biomolecular behavior or interactions relies on the ability to record these current blockades with superior fidelity, which poses great challenges with respect to the noise characteristics of the solid-state device. Here we present systematic studies addressing the current noise of solid-state nanopores for translocation experiments. Pores with diameters <10 nm have been fabricated in $Si_3N_4$ membranes by e-beam lithography and subsequent shrinking in a transmission electron microscope. The electrical characteristics of the nanopore chips in aqueous pH-buffered saline solutions are studied using electrochemical impedance spectroscopy (EIS), cyclic voltammetry, and potential step methods. Equivalent circuit models to represent the nanopore device are proposed based on the obtained data. The frequency dependence of the current noise is recorded with spectral analyzers and discussed within the extracted equivalent circuit models. Within this framework, we investigate the influence of various parameters on the electrical noise: (i) chip designs with different membrane dimensions are realized by combining optical and e-beam lithography with feedback-etching methods, (ii) surface passivation using silicone elastomers and photo-resists are compared, (iii) the composition, salinity, and pH value of the buffer solution is examined. Our results allow us to identify the contribution of various capacitances and dielectric losses across the chip to the measurement noise and suggest guidelines for low-noise translocation recordings.

**BI-ThP10 Fabrication and Chemical Surface Treatment of Solid State Nanopores in SiN Membranes**, ***M. Firnkes**, D. Pedone, G. Abstreiter, U. Rant*, Technical University Munich, Germany

Solid state nanopores attracted broad attention in recent years as a tool to study biological molecules like DNA or proteins. In these experiments, the translocation of the molecule through the nanopore is detected by a blockade of the ionic current across the pore. Up to now solid state nanopores are mainly directly drilled into a freestanding silicon nitride membrane via an intense e-beam. Here we report a new pore fabrication technique. Single nanopores are processed in silicon nitride membranes by e-beam lithography and feedback-controlled wet chemical etching, followed by TEM induced shrinking. Moreover we present current noise data showing the influence of various chemical treatments of the pore surface. Starting with a (100) silicon chip of 200 µm thickness, which features 50 nm silicon nitride coatings on both sides, we use optical lithography to form an etch mask on the chip's back side for anisotropic etching of the silicon with KOH. Subsequently we utilize e-beam lithography on the front side to open holes of 40 – 50 nm in the silicon nitride. In the next step the silicon is etched by KOH resulting in a pyramidal shaped undercut of the small holes on the chip front side. During a second KOH etching process from the backside only, we observe the time dependence of the electrical current across the silicon chip. The etching is stopped when a certain current threshold indicates the opening of the pyramid. In this way the pyramid is truncated in a controlled manner. This leads to a 5 x 5 µm freestanding silicon nitride membrane containing the pore. To get the desired pore size we shrink the pores using a TEM. Electrical noise analysis data is presented showing the influence of small membrane sizes resulting from feedback-controlled etching. In addition we studied the influence of the surface termination on wetting properties and electrical noise. In this context we applied both oxidizing (HF) as well as reducing agents (piranha, oxygen plasma) to change the surface properties of the nanopores. Our results show the benefits of the combination of feedback chemical etching and standard nanopatterning techniques on the electrical noise and indicate how current recordings can be obtained with low noise by a chemical treatment of the nanopore.

**BI-ThP11 Determination of Protein Charge with Switch DNA Bio-Sensors**, ***J. Knezevic***, *W. Kaiser, E. Pringsheim, G. Abstreiter, U. Rant*, Technische Universität München, Germany

In the recent past, switchable DNA layers have been established as promising candidates for biosensors.[1] Here, the efficiency and dynamics of the electrically induced conformation-switching of surface tethered DNA molecules are used as the sensing parameters. The detection of DNA and proteins (antibodies and antibody fragments) has been demonstrated. Moreover, the size of the captured protein targets could be determined from the switching dynamics on-chip. However, the influence of the proteins' charge remained unclear in these experiments. Here we report on DNA-switching bio-sensing experiments, where the influence of the protein charge was investigated on the basis of the avidin/ streptavidin/ neutravidin-model system. The modulation amplitude of the switching DNA layer was probed electro-optically at low frequencies of the driving electrical signal. The switching kinetics of the tethered molecules were analyzed by frequency resolved measurements. In addition, the double layer charging process was evaluated by impedance measurements. The proteins' charge was varied on-chip by altering the solution pH value. In complementary measurements, the target proteins were characterized regarding their charge and size by dynamic-light scattering. The correlation between the protein charge and size and the low-frequency switching behavior is evaluated. Further, the influence of the protein charge and size on the switching dynamics is described. The results are discussed within the framework of classical electrostatic screening models. Finally, we elucidate the possibility to employ switchable DNA layers for the charge-sensitive detection and characterization of proteins, as well as biomolecules in general.

[1] Rant et al., PNAS 2007, vol. 104, pp. 17364-17369.

**BI-ThP12 Surface-enhanced Raman Scattering from Controlled Nanoparticle System**, ***S.Y. Chen***, *D.S. Sebba, A.A. Lazarides*, Duke University

We present a theoretical and experimental study of surface-enhanced Raman scattering from core-satellite nanoparticle assemblies of known structure in the solution phase. The detectability of the Raman signal is attributed to enhanced electromagnetic fields localized between plasmonically coupled core and satellite metal nanoparticles. Design of the structures was accomplished using near field calculations based upon Generalized Mie theory, a theory that accurately accounts for multipolar coupling within clusters of spherical particles. Assembly structures are identified on the basis of positions of hot spots and overlap of plasmon resonance frequencies with Raman excitation spectra and available laser lines. Core-satellite structures are assembled using DNA linkers and characterized by transmission electron microscopy (TEM). The control of field strength and plasmon frequency provided by the coupled particle system is expected to provide insight into SERS signaling of use in application of SERS to biomolecule sensing.

**BI-ThP13 Magnetic Tweezer Sensor for Ensemble Binding Events of Nonmagnetic Particles**, ***R.M. Erb***, *R.E. Ducker, S. Zauscher, B.B. Yellen*, Duke University

Current methods to measure molecular binding strengths include force pulling methods such as atomic force microscopy and optical tweezing. These methods are greatly limited in their throughput, requiring molecular fishing and individual particle targeting that produces binding data on the order of minutes or hours. To overcome these deficiencies, the authors have developed a magnetic system that allows for fast ensemble measurements of thousands of single particle-substrate bonds simultaneously using a High Gradient Magnetic Separation (HGMS) system. The described system is a dense array of micron-size ferromagnetic thin islands on a substrate. These magnetic arrays offer the ability to apply very strong particle forces that can be in the range of tens of nanonewtons, orders of magnitude higher than most optical or electrical systems. Additionally, this system can be used to apply forces on nonmagnetic particles by submerging them in biocompatible magnetic fluids, a technique known as "inverse" magnetophoresis. The ferrofluid causes the nonmagnetic particles to behave as magnetic holes allowing for particle-substrate bonds to be broken through the islands' applied magnetic force. The authors have extended this system onto the surface of a quartz crystal microbalance (QCM) sensor, which allows for the accurate sensing of ensemble particle movement. To test this system, the authors use a mixed self-assembled monolayer of biotin and oligoethylene glycol and selectively bind streptavidin coated particles to the magnetic islands. Using the magnetic islands and an external magnetic field, streptavidin particles are attracted to a preprogrammed edge of the islands and are allowed to undergo molecular binding with the surface. As an opposite external field is applied, the particles will be pulled en masse to the opposite side of the islands, a movement that can be sensed and analyzed by the QCM. Through knowing the applied magnetic forces, this system allows for the ensemble quantification of bond dissociation between any chemically active particle and substrate.

**BI-ThP14 Nanoparticle Thermoplasmonic Modulation**, *R.H. Farahi*, ***A. Passian***, *A.L. Lereu, T.G. Thundat*, Oak Ridge National Laboratory, *Y. Jones*, Alcorn State University

Single particle thermo-optical properties are increasingly important in applications such as therapeutics, nano devices, and alternative energy sources. In these applications, the temperature dependent electronic characteristics play a role in the feasibility, efficiency, and the functionality of the intended system. We present an investigation of the thermal properties of gold nanoparticles on a quartz substrate using optical excitation of surface plasmons. The surface deformation, in the region of the localized optical modulation of the surface plasmons, is studied as a function of frequency, power, and polarization. A non-linear frequency and power dependence is observed for the nanostructure system as a result of the thermoplasmonic processes including the volumetric deformations. A threshold power for the observation of the modulation is estimated and is in good agreement with theoretical and computational results.

**BI-ThP15 Where DNA and Plasmonics Meet- An Investigation into Cooperative Molecular Recognition at a DNA Nanostructure-Metal Interface**, ***E.R. Irish***, *T.H. LaBean, A.A. Lazarides*, Duke University

Recent work in assembly of complex DNA nanostructures has demonstrated the effectiveness with which the non-covalent forces of DNA hybridization can drive formation of a topologically rich set of engineered DNA nanostructures. These DNA nanostructures can be used as structural components within a variety of complex nanosystems, including integrated systems for molecular detection. With the advances in the design and solution phase assembly of novel addressable DNA nanostructures, there is a need for the development of new techniques for controlling deposition of the structures on surfaces. The objective of this research is to investigate thermodynamic and kinetic control of interactions between DNA nanostructures and oligonucleotide functionalized gold films. In this research, surface plasmon resonance (SPR) is used for real-time monitoring of the hybridization of DNA structures on oligonucleotide functionalized gold films. Kinetic and thermodynamic parameters derived from the SPR reflectivity data are used to evaluate the effect of multivalence on the strength of interaction. Kinetic measurements, such as the association and dissociation rates, are determined through the monitoring of the SPR response to hybridization as a function of concentration. Ultimately, understanding of the kinetic and thermodynamic parameters that characterize multivalent interactions between DNA nanostructures and gold films will enable engineering of interactions at soft/hard matter interfaces. It is anticipated that the new tools for integrating soft matter on patterned templates will prove useful in future applications of DNA nanostructures that require organization of the soft matter.

## Electronic Materials and Processing
## Room: Hall D - Session EM-ThP

## Electronic Materials and Processing Poster Session

**EM-ThP1 Effect of Water Immersion and Surface Compositional Profile of Photoacid Generator Molecules in Photoresist Materials**, ***S. Sambasivan***, Suffolk Community College, *V.M. Prabhu, D.A. Fischer*, National Institute of Standards and Technology, *L.K. Sundberg, R.D. Allen*, IBM Almaden Research Center

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to quantify the surface composition and depth profiling in the top 2 to 6 nm range of photoacid generators (PAG) in thin film photoresist materials. By considering model compositional profiles, NEXAFS distinguishes the surface molar excess within the top 6 nm from the bulk. A surface enriched system, triphenylsulfonium perfluorooctanesulfonate (TPS-PFOS), is contrasted with a perfluorobutanesulfonate (TPS-PFBS) photoacid generator, which displays an appreciable surface profile within a 6 nm segregation length scale. A comparative study of the surface composition of PAG (TPS-PFOS, TPS-PFBS and TPS-Triflate) in photoresist system before and water immersion was monitored via NEXAFS. Results reveal that the loss of PAG occurs after the water immersion in all the three different PAG system examined. Detailed quantification of the PAG loss due to water immersion was seen to critically depend on the size of the PAG and its solubility in water. TPS-PFOS photoacid generator largest in size despite its least solubility in water showed the maximum loss after water immersion followed by TPS-PFBS and TPS-Triflate. These results, while applied to 193-nm photoresist materials, highlight a general approach to quantifying NEXAFS partial electron yield data and find application to immersion lithography fundamentals.

### EM-ThP2 Direct Evidence for Post-Crystallization Germanium Precipitation in Thin Films of Phase-Change Material $Ge_{15}Sb_{85}$, *C. Cabral, Jr.*, *L. Krusin-Elbaum,* IBM T.J. Watson Research Center, *S. Raoux, V.R. Deline,* IBM Almaden Research Center, *J. Bruley, A Madan, T.L. Pinto*, IBM Hudson Valley Research Park

We present evidence for the instability in the crystalline metallic phase of eutectic phase-change $Ge_{15}Sb_{85}$ thin films considered for integration into nonvolatile embedded memory cells. Te-free phase-change materials, owing to a combination of higher crystallization temperatures and the absence of easily diffusing chalcogen atoms, offer an advantage over the ternary chalcogenides, provided that the material is stable throughout the switching process. We find that while the amorphous (semiconducting) phase is robust until $Ge_{15}Sb_{85}$ film's crystallization into a rhombohedral structure at 240ºC, at 350ºC, Ge rapidly precipitates out, aggregating at the film's grain boundaries and interfaces. Ge precipitation, visualized directly with transmission electron microscopy and in-situ x-ray diffraction, is found to be exothermic by differential scanning calorimetry, and is found to affect films' reflectivity, resistance, and stress. Such changes could impact switching reliability, with additional doping required to minimize the precipitation process.

### EM-ThP3 Development of a Polycrystalline Zinc Oxide Scintillator for Radiation Detection, *D.M. DeVito*, *J.S. Neal, B.L. Armstrong,* Oak Ridge National Laboratory, *M. Hong,* University of California - Davis, *B. Kesanli, J.O. Ramey, J.Y. Howe,* Oak Ridge National Laboratory, *X. Yang, N.C. Giles,* West Virginia University, *Z.A. Munir,* University of California - Davis, *L.A. Boatner*, Oak Ridge National Laboratory

N-type doped ZnO is an ideal scintillator for use as an alpha particle detector due to its high light output, chemical stability, and sub-nanosecond decay times. ZnO, being a non-cubic material, has seen little success in producing the highly transparent polycrystalline bodies needed for scintillator applications. In this work, ZnO:Ga and ZnO powders were pressed into high density (>98%) polycrystalline bodies by hot uniaxial pressing and spark plasma sintering. These samples showed both photoluminescence and emission under alpha particle exposure. Investigation of the sample microstructure showed substantial grain growth. Samples also showed a high degree of translucency after post-sintering heat treatments. Additional processing results will also be included.

### EM-ThP4 Structure and Optical Behavior of Sputter Deposited Hafnia-Alumina Nanolaminate Films, *E.E. Hoppe*, *M. AlMomani, C.R. Aita*, University of Wisconsin-Milwaukee

Nanolaminate films of polycrystalline $HfO_2$ and amorphous $Al_2O_3$ were grown by reactive sputter deposition on unheated fused $SiO_2$ and the nascent oxide of <111> Si. Many different bilayer architectures were examined. The films were air annealed at 573 K to 1273 K, and analyzed by double angle x-ray diffraction and ultraviolet-visible spectrophotometry. X-ray diffraction showed the amount of monoclinic $HfO_2$ (the bulk equilibrium phase) decreased with decreasing $HfO_2$ layer thickness. Previous high resolution transmission electron microscopy results[1] showed that the initial $HfO_2$ phases present in ultrathin layers were tetragonal and orthorhombic, consistent with a finite crystal size effect. Annealing of the as-grown nonmonoclinic structure at temperature up to 973 K produced no gross structural change. Annealing at 1173 K produced a metastable mixed cation tetragonal phase, $Hf_{1-x}Al_xO_{2-z}$, that is isomorphous with tetragonal $HfO_2$. This mixed cation phase became unstable at 1273 K and phase-separated into monoclinic $HfO_2$ and amorphous $Al_2O_3$. In all cases, the fundamental optical absorption edge was found to consist of two distinct regions with respect to incident photon energy. Significant O 2p -> Hf 5d interband absorption occurred at energy $E \geq 6.2$ eV. For $E < 6.2$ eV, films with nonmonoclinc structure retained a (desirable) featureless optical absorption edge despite further (nano)crystallization, including the formation of $Hf_{1-x}Al_xO_{2-z}$. Films with a monoclinic structure developed a pre-gap absorption band found to be characteristic of the seven-fold Hf-O coordination in the single layer monoclinic $HfO_2$.[2] We relate this undesirable pre-gap absorption band to self-trapped excitons that can form in the monoclinic structure.[3]

[1] E.E. Hoppe, M. Gajdardziska-Josifovska, and C.R. Aita, Appl. Phys. Lett. 91, 203105 (2007).

[2] E.E. Hoppe, R.S. Sorbello, C.R. Aita, J. Appl. Phys. 101, 123534 (2007).

[3] D. Muñoz Ramo et al. PRL 99, 155504 (2007).

### EM-ThP5 Properties of Mn Doped ZnO Hollow Nanosphere Structures, *D.-R. Liu*, *C.-C. Kei, C.-Y. Su, W.-C. Chen*, National Applied Research Laboratories, Taiwan

Diluted magnetic semiconductors (DMS) have recently attracted considerable attention due to their potential applications for spintronic devices, such as spin-valve transistors, nonvolatile memory, and magneto-optical switches. ZnMnO is one of the most promising DMS materials due to its predicted above room temperature ferromagnetism. In this study, Al2O3 layer was conformally deposited on the surface of polystyrene (PS) nanoshpere by atomic layer deposition (ALD). After removal of PS nanosphere by heating, alumina hollow nanospheres were formed. Then the (1-x)Zn(x)MnO hollow nanosphere were grown by Nd:YAG pulsed laser deposition(PLD). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) were employed to characterize the surface properties of these samples. The high-resolution x-ray diffraction was used to evaluate the crystal quality. The magnetic properties of the (1-x)Zn(x)MnO hollow nanosphere were measured by a superconducting quantum interference device (SQUID) magnetometer. Photoluminescence (PL) spectroscopy and spectrometer were used to characterize the optical properties. The results show that the properties of Mn doped ZnO hollow nanosphere strongly depend on the size of nanosphere.

### EM-ThP6 Electrical Properties of Atomic Layer Deposited ZnO Thin Film Transistor with Various Channel Layer Thickness, *W. Jeong*, *S. Bang, S. Lee, S. Jeon, S. Kwon, H.T. Jeon*, Hanyang University, Korea

Wide band gap II-VI compound semiconductors have attracted much attention because of many potential applications for optoelectronic devices. Among these, ZnO thin films have been particularly interesting due to their potential applications in optoelectric devices, such as light-emitting diodes, laser diodes, and transparent thin film transistor. Especially, ZnO-based thin film transistors (TFTs) have been intensively studied for flexible electronics, replacing conventional amorphous-Si TFT. Recently, there have been several reports on the fabrication of ZnO TFTs by means of rf magnetron sputtering, pulsed laser deposition, and chemical solution process. These methods need high process temperature or additional annealing process to obtain good transistor properties such as high mobility, low operation voltage. However, high temperature process is not suitable to apply for flexible substrates or organic dielectrics. Hence, we choose atomic layer deposition (ALD) method because ALD offers several advantages over the other techniques such as large area capability and good growth control in terms of homogeneity, composition, and thickness. Moreover, ALD process can be performed at low temperature. These merits are fundamental for a wide variety of applications requiring low thermal budgets. However, atomic layer deposited ZnO films exhibit high carrier concentration ($n \sim 10^{18}$ $cm^{-3}$). The high channel carrier concentration in the oxide semiconductors is not suitable for TFT applications. Therefore, it is necessary to control the carrier concentration in order to build good quality ZnO-TFT. In this study, we varied thickness of ZnO in order to find optimal condition for thin film transistor. ZnO film on $SiO_2$/p-type Si substrate was deposited by ALD method using diethylzinc (DEZn) and H2O at 110 °C and the thickness of ZnO film were varied from 40 nm to 70 nm as a function of ALD cycles. The crystallographic orientation of the ZnO films was determined by an X-ray diffractometer (XRD) with Cu Ka radiation and the film morphology was analyzed by Atomic force microscopy (AFM) measurements. Device characterization was carried out at room temperature in the dark using an Agilent B1500A Semiconductor Analyzer. As a result, Ion/Ioff ratio was observed in $10^2$~$10^6$, saturation mobility was observed in 0.02 ~ 1.4$cm^2$/Vsec.

### EM-ThP7 Characterization of P-Si/$SiO_2$/N+Si Devices with Various Thickness of $SiO_2$, *S.M. Lee*, *B.I. Son, K.H. Eum, I.S. Chung*, Sungkyunkwan University, Korea

We attempted to evaluate n+Si/SiO2/p-Si devices as a function of the thickness of SiO2. The thickness of SiO2 were varied from 2 nm to 5 nm. The breakdown of SiO2 layer in n+Si/SiO2/p-Si structure cause the device appears as pn+ junction diode. The simulated results using Silvaco TCAD also indicate that the currents of n+Si/SiO2/p-Si structures increase exponentially with respect to the applied voltage in the forward bias region. In addition, as the SiO2 breakdown is getting serious, the current-voltage curve moves toward the that obtained from ideal pn+ junction diode. The ratio in the current at 1.5 V between the breakdown device and the non-breakdown device reveals higher than 10000. The off state current in n+Si/SiO2/p-Si structure was simulated based on the direct tunneling model. The fabricated devices reveals similar characteristics. However, as the thickness of SiO2 layer decreases, the breakdown distribution and reliability tends to show worse results.

**EM-ThP8 Role of Adsorbates in Surface Electron Accumulation on InN Films**, *R.P. Bhatta, A.R. Acharya,* ***B.D. Thoms****, M. Alevli, N. Dietz*, Georgia State University

The presence of surface electron accumulation on a semiconductor has been shown to affect the properties of metallic contacts and may be important in determining other properties of devices. Adsorbates have been shown to affect the electron density on InAs surfaces, however, the effects on the surface electron concentration for InN have not been established. In this work, the effects of adsorbates on surface electron accumulation for N-polar InN have been studied by high resolution electron energy loss spectroscopy (HREELS). By varying the energy of the incident electrons the probing depth can be varied. Shifts in the energy of the conduction band plasmon indicate differences in plasma frequency and therefore differences in free carrier concentration as a function of depth from the surface. By this method it is shown that hydrogen-terminated N-polar InN exhibits surface electron accumulation. Heating InN for 15 minutes at 425°C desorbs the surface hydrogen without surface damage or film decomposition. HREELS of bare N-polar InN indicates the presence of surface electron accumulation and confirms that no surface indium is present. These results indicate that surface electron accumulation is not due to indium-indium bonding and is not affected by the presence or absence of surface hydrogen, but may instead be intrinsic to the N-polar InN surface. The effects of other adsorbates, such as oxygen, will also be discussed.

**EM-ThP9 Effect of TCO Buffer Layer on the Growth of InN Film by MOMBE**, ***W.-C. Chen,*** National Applied Research Laboratories, Taiwan, *S.-Y. Kuo,* Chang Gung University, Taiwan, *H.-C. Pan,* Gintech Energy Corporation, Taiwan, *F.-I. Lai,* Yuan Ze University, Taiwan, *C.-N. Hsiao*, National Applied Research Laboratories, Taiwan

In this paper, wurtzite structure Indium nitride films on TCO layer was examined. InN films were grown on highly-quality of TCO buffer layer by UHV-plasma assisted metal-organic molecule beam epitaxy system. We have studied influence of to growth temperature by their structure, surface morphology and optical properties. The InN films has been characterized in detail using X-ray diffraction (XRD), field emission scanning electron microscopy (FE-SEM), Transmittance electron microscopy(TEM),Hall effect. The surface roughness was obtained from SEM measurements with increased growth temperature. Furthermore, a pronounced two-dimensional growth mode was observed at the growth temperature of 500 ℃, and InN films highly oriented to the c-axis were obtained by optimizing growth conditions in the direct growth on TCO buffer layer. TEM images show these InN films are single phase wurtzite crystals with preferred orientation along the c axis. Our results indicated that the growth temperatures of 500-550 ℃ were beat to achieve high quality InN films.

**EM-ThP10 Synthesis of Ordered Arrays of (Ba$_{0.6}$,Sr$_{0.4}$)TiO$_3$ Nanotubes**, ***G.H. Kim****, K.T. Kim, C.I. Kim,* Chungang University, Korea, *Y.K. Yoon*, University at Buffalo, the State University of New York

(Ba$_x$,Sr $_{1-x}$)TiO$_3$ (BST) ferroelectrics exhibit high dielectric permittivity and have been widely investigated both in films and ceramics. Using BST ferroelectric structures, manufacturing highly integrated memory device is possible. Recently, one dimensional nanostructures, such as nanotube and nanofiber, have been intensively studied because of their unique structure and properties. However, the BST nanotube arrays have not been widely studied yet because of fabrication difficulty and its properties are not reported. The main aim of this work includes the fabrication and investigation of structural BST nanotube arrays prepared using the sol-gel method in an anodized nanoporous aluminum oxide template. The perovskite phase has been obtained as a function of the annealing temperature from 450 to 700 $^{o}$C for 1h. The crystalline structures of the BST nanotubes arrays have been analyzed by X-ray diffraction. The surface and cross-sectional microstructures of BST nanotubes arrays are examined using scanning electron microscopy and transmission electron microscopy. The electrical P-E curve (hysteresis loop) of the BST nanotube array are illustrated.

**EM-ThP11 Fabrication of Cerium Oxide Nanopillars for Oxygen Gas Sensor by Nanosphere Lithography**, ***P.-J. Ko****, J.-S. Park, H.-Y. Na,* Chosun University, Korea, *N.-H. Kim,* Chonnam National University, Korea, *W.-S. Lee*, Chosun University, Korea

Cerium oxide (CeO$_2$) is one of the most widely used materials for the oxygen gas sensors. Sensing properties of CeO$_2$ is required to be improved by the fabrication to nanometer-scaled structure. The well-arrayed nanopillars of CeO$_2$ in a large area were fabricated by nanosphere lithography and oxygen plasma etching process. The spin coated CeO$_2$ thin films on silicon substrates by Sol-Gel method were prepared. Polystyrene beads of 100 nm were arrayed orderly on CeO$_2$ thin films and they were ashed by oxygen plasma for decreasing the size of well-arrayed polystyrene beads. Plasma etching of CeO$_2$ thin films was performed by inductively coupled plasmas (ICP) with the ashed polystyrene beads as a mask. The high-density nanometer-scaled pillars of CeO$_2$ were successfully fabricated with a diameter of 50 nm and the distance of 50 nm between the neighboring beads. The effects of the fabrication of CeO$_2$ nanopillar on the sensing properties were also investigated. The improved sensing properties of CeO$_2$ for oxygen sensors were obtained after fabrication of nanopillar of CeO$_2$ by the nanosphere lithography of polystyrene beads. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2007-412-J02003).

**EM-ThP12 Influence of Acid Etching of MgAl$_2$O$_4$ (111) Substrate on the Deposition of ZnO Thin Film by MOCVD**, ***G.Y. Jhan****, Y.J. Chen, H.Y. Lai, J.H. Du, J.H. Liang*, National Dong Hwa University, Taiwan

MgAl$_2$O$_4$ (111) has lower lattice mismatch than c-plane sapphire with ZnO epilayer, so it is possible for ZnO film deposited on MgAl$_2$O$_4$ to obtain better quality than on c-plane sapphire. However, MgAl$_2$O$_4$ (111) has two kinds of sublattice of oxygen layer. Although surface energies of two kinds of sublattice of oxygen layer are similar, the sublattice constants of oxygen layers are different. Since the difference of oxygen sublattice constant could affect ZnO film epitaxy quality on MgAl$_2$O$_4$ (111), we should control surface of MgAl$_2$O$_4$ (111) to expose the proper oxygen sublattices for ZnO film growth. In this research, we studied influence of H$_2$SO$_4$ and H$_3$PO$_4$ etching of MgAl$_2$O$_4$ (111) substrate on the deposition of ZnO thin film by MOCVD. The chemical etching of MgAl$_2$O$_4$ was performed with H$_2$SO$_4$ and H$_3$PO$_4$ respectively to obtain different surfaces of MgAl$_2$O$_4$ (111). The ZnO film was deposited on pretreated MgAl$_2$O$_4$ (111) at the growth temperature of 350°C. By SEM、XRD and PL analysis, the specimen of H$_3$PO$_4$ etching has better quality than specimen of H$_2$SO$_4$ etching at the growth temperature of about 350°C. These results imply that different surfaces were created by using H$_3$PO$_4$ and H$_2$SO$_4$. We proved that ZnO film has good quality on H$_3$PO$_4$ etched MgAl$_2$O$_4$ (111) substrate.

**EM-ThP13 Self-Limiting Growth of Semiconductor Grade Zinc Oxide at Low Temperature by Pulsed Pecvd and Plasma-Enhanced Atomic Layer Deposition**, ***P. Rowlette****, C.G. Allen, O. Bromley, D.N. Richards, A. Dubetz, C.A. Wolden*, Colorado School of Mines

Self-limiting growth of ZnO was accomplished using both pulsed plasma-enhanced chemical vapor deposition (PECVD) and plasma-enhanced atomic layer deposition (PE-ALD) at temperatures ranging from 25–155 ºC. This work explored the suitability of dimethyl zinc (DMZ, Zn(CH3)2) as an alternative to the commonly used diethyl zinc (DEZ, Zn(C2H5)2) precursor. Mass spectrometry shows that DMZ is less reactive than DEZ, which may be advantageous for self-limiting growth of semiconductor grade ZnO. In pulsed PECVD DMZ and O2 were both supplied continuously, while in PE-ALD the DMZ was delivered in pulses separated by purge steps. Films were characterized using spectroscopic ellipsometry, Fourier transform infrared (FTIR) spectroscopy, photoluminescence (PL), Hall measurements, energy dispersive spectroscopy (EDS), and X-ray diffraction (XRD), atomic force microscopy (AFM), and field emission scanning electron microcopy (FE-SEM). Deposition rates scaled with DMZ exposure during pulsed PECVD films, and could be tuned over a large range (1.5 – 6.0 Å/pulse). The PE-ALD growth rate saturated at 2.9 Å/cycle for DMZ exposures >50 mTorr*s. Deposition rates increased exponentially for pulsed PECVD films as a function of substrate temperature, while PE-ALD displayed a constant rate within a temperature window of 85 to 120 ºC. With the substrate temperatures elevated above 70 ºC, impurities related to carbon and hydroxyl groups were attenuated below the detection limit of FTIR for both deposition modes. EDS analysis showed that all films were stoichiometric. At low temperatures pulsed PECVD films were amorphous, and became polycrystalline at higher temperatures with a preferred orientation in the (100) direction. PE-ALD produced polycrystalline films with a (100) texture at room temperature, with the preferred orientation switching to the (002) direction as the substrate temperature was increased. Changes in orientation were accompanied by alterations in surface morphology. The as-deposited films were semiconductor grade, with resistivity values ranging from of 1 – 20 W-cm. The high quality of the films was confirmed by strong band edge emission in room temperature PL experiments. Films deposited at room temperature also showed strong emission from oxygen vacancies, however emission from these defects was attenuated for substrate temperatures ? 120 ºC.

# Magnetic Interfaces and Nanostructures
# Room: Hall D - Session MI-ThP

## Magnetic Interfaces and Nanostructures Poster Session

**MI-ThP1 Fabrication of Permalloy Nanowire Structure to Realize a Magnetic Analog to a Coupled Pendulum**, ***M.S. Seo****, S.U. Cho, C.W. Yang, Y.D. Park*, Seoul National University, Republic of Korea

We report on the fabrication of NiFe nanowires structures to demonstrate a magnetic analog to a coupled pendulum. Coupled high-frequency resonators have already been demonstrated in magnetic nanostructures.[1] Recently, an analog to a mechanical pendulum system has been applied to measure the mass of a domain wall in NiFe nanowires.[2] We have designed a NiFe nanowires structures akin to two semicircular arc segments, arranged with a mirror symmetry about the tangent, with a separation distance ≤ 100 nm. From symmetry arguments, the magnetostatic forces couple the domain walls formed at the apex of each semicircular segment. By varying the separation distances as well as driving current densities, the coupling strengths can also be modulated. The structures are patterned by e-beam lithographic techniques on a UHV sputter deposited NiFe. Each segment is probed electrically allowing for driving force as well as to detect current induced resonance effects on domain wall resistance for each segment. Along with experimental data at the extremes of coupling strengths, we will also compare the results with finite element analysis modeling.

[1] S. Kaka et al., Nature 437, 389 (2005); F.B. Mancoff et al., ibid 437, 393 (2005).

[2] E. Saitoh et al., Nature 432, 203 (2004).

**MI-ThP2 Magnetic Dot Polarity Switching Via Current Generated Magnetic Fields**, ***M.R Rao****, J.C Lusth, S. Burkett, Y.K Hong*, University of Alabama

This paper describes the manipulation of the magnetic alignment of nickel dots using a magnetic field generated by current flowing through an aluminum wire. This architecture has the potential to operate as a memory device offering low power dissipation, high integration density, and room temperature operation. The aluminum wire had dimensions of 250 nm in thickness, 10 µm in width, and 40 µm in length. The nickel dots were formed by electron beam lithography and had a thickness of 100 nm and diameter ranging from 200 nm to 500 nm. The dots were deposited in an array such that some dots lay on the wire and some dots lay nearby. A magnetic field was applied to the ferromagnetic dots by passing current through the aluminum wire. Switching of the dots magnetic polarity was observed using magnetic force microscopy (MFM). MFM cantilever phase and amplitude images were used to identify the reversal of the polarity of the dots. Contrast changes were detected upon reversing the current flow. The fabrication of this device concept is relatively simple. Microscale aluminum wires are patterned with conventional photolithographic techniques while a separate electron beam lithography step is used to pattern nickel dots at variable position across the wire. The nickel dot's magnetic field is oriented in a specific direction after passing electric current through the aluminum wire. On reversal of the current, the dot's magnetic field is oriented in the opposite direction. These directions can be treated as a logic '1' or logic '0'. The orientation of the magnetic dots remains even after switching off the current. This indicates potential operation as a memory device.

# Nanomanufacturing Focus Topic
# Room: Hall D - Session NM-ThP

## Nanomanufacturing Poster Session

**NM-ThP1 Nanoscale Release Effect of Antisticking Layer for Nanoimprint Resin Characterized by Scanning Probe Microscopy**, ***M. Okada***, University of Hyogo, Japan, *M. Iwasa*, SII Nanotechnology Inc., *K. Nakamatsu, K. Kanda, Y. Haruyama, S. Matsui*, University of Hyogo, Japan

Nanoimprint lithography (NIL) has a capability to fabricate nanostructure devices with a high-throughput and a low cost. Nanoimprint lithography molds are coated with an antisticking layer so that they do not come in contact with the adhesion of replication materials. Friction and adsorption occurs between the nanostructure mold and nanoimprint resin during demolding. Measuring the nanoscale frictional force and adsorptivity between the antisticking layer and resin is therefore important. In this paper, we measured the nanoscale frictional force and adsorptivity between a cantilever and nanoimprint resin by scanning probe microscopy (SPM) using Si cantilevers with and without antisticking layer. We used a self-assembled monolayer (SAM) consisting of a silane-coupling agent with fluoropolymer (OPTOOL DSX: Daikin industries) as an antisticking layer. The thermoplastic resin (PMMA; OEBR 1000: TOKYO OHKA KOGYO Co.) and the photosensitive resin (PAK-01: Toyo Gosei Co.) were also used. In the SPM measurement using Si cantilever, results were obtained between the Si and NIL resin. On the other hand, the measurement results between the antisticking layer and resin were obtained by SPM using the cantilever with an antisticking layer. The frictional force of PMMA and PAK-01 measured using the cantilever with an antisticking layer are respectively 0.7 and 0.6 times lower than those using the cantilever without the antisticking layer. The adsorptivity of PMMA and PAK-01 measured by SPM using the cantilever with an antisticking layer are 0.4 and 0.6 times lower than those using the cantilever without the antisticking layer. These results show that SPM measurement using the cantilever with and without antisticking layers can be applied to evaluate the nanoscale release effect between an antisticking layer and nanoimprint resins.

**NM-ThP2 Ultrasonic Nanoimprint on Engineering Plastics**, ***H. Mekaru****, M. Takahashi*, National Institute of Advanced Industrial Science and Technology (AIST), Japan

We have developed a new ultrasonic nanoimprint technology that is superior to the current thermal and UV nanoimprint technologies. In this method an ultrasonic vibration is impressed in the direction of loading force during a molding operation at room temperature. Our nanoimprint system employed a magnetostriction actuator capable of generating ultrasonic vibration with frequencies and amplitudes ranging from DC to 30 kHz, and from 0 to ± 30 µm respectively. Here an electroformed-Ni mold consisting of dot and line/space patterns with a minimum width of 500 nm was employed to endure the mechanical stress by the ultrasonic vibration. The mold was mounted onto the ultrasonic generator with a photoresist. We report on the results of ultrasonic nanoimprinting on various engineering plastics. At first, several optimized imprinting conditions were investigated by using polyethylene terephthalate (PET, Tg = 75 °C) with a comparatively low glass transition temperature (Tg) in engineering plastics. When the frequency of the ultrasonic vibration was varied in steps of 0.1 - 10 kHz, and the amplitude in steps of 0.5 - 3 µm, the height of the imprinted pattern was found to rise with the increase in the frequency and the amplitude. In this case, a rubber sheet serving as a buffer was interposed between the thermoplastic sheet and the bottom loading stage to keep the contact force of mold patterns on the thermoplastic uniform. By employing four kinds of rubbers the hardness of the buffer material was changed to 32, 57, 80, and 90 °. When the low repulsion rubber sheet in the hardness of 57 ° was used without ultrasonic vibration, the height of the imprinted pattern reached a maximum. However, in the presence the ultrasonic vibration the optimized buffer material was a sheet of urethane in the hardness of 90 °. Then under those same molding conditions, polycarbonates (PC, Tg = 150 °C) and polymethyl methacrylates (PMMA, Tg = 105 °C) were successfully imprinted and the pattern was observed by SEM; although in the absence of the ultrasonic vibration it was not possible to mold. The heights of the imprinted pattern were measured to be 1 µm in PET, 750 nm in PMMA, and 370 nm in PC. The assisting effect of the ultrasonic vibration was found to be inversely proportional to Tg. Therefore, it is inferred that the thermoplastic was softened locally with the frictional heat generated by the ultrasonic vibration.

**NM-ThP3 Atomic Layer Etching of Cl-Adsorbed GaAs by Using a Low-Angle Forward Reflected Ne Neutral Beam**, ***W.S. Lim****, J.B. Park, G.Y. Yeom*, Sungkyunkwan University, Korea

GaAs compound-based semiconductors are currently investigated for various devices such as high efficiency solar-cell, high mobility electronic devices, optical devices, etc. due to direct band structure, high electron mobility, high operating temperature range, etc. For the processing of gallium arsenide (GaAs), conventional dry etching processes such as chlorine-based inductively-coupled plasma (ICP) are used but they tend to cause physical damage on the surface due to the irradiation of high energy ions during the etching, and which results in the degradation of the devices. Therefore, the removal of surface damage during the processing is essential and, among the various dry etching processes, atomic layer etching (ALET) has been studied to realize atomic scale etch-rate controllability of GaAs without physically damaging the surface of GaAs. In this study, the characteristics of ALET for (100)/ (111) GaAs have been investigated as functions of $Cl_2$ pressure during the adsorption stage and Ne neutral beam irradiation dose during the desorption stage. By using the Ne neutral beam dose and the $Cl_2$ pressure higher than the critical values of $3.03\times10^{16}$ atoms/cm$^2$•cycle and 0.4 mTorr, respectively, one monolayer etching condition of 1.41 Å/cycle for (100) GaAs and 1.63 Å/cycle for (111) GaAs could be obtained through the adsorption of one monolayer of $Cl_2$ during the adsorption stage and desorption of all of the chlorides formed on the surface by the sufficient Ne neutral beam irradiation. At the monolayer etching conditions, the surface roughness was the lowest and was similar to that of as-received GaAs. Therefore, the use of ALET condition enabled us to control the etch depth with an atomic-scale precision without damaging the surface physically or chemically.

**NM-ThP4 Fabrication of a Highly-Oriented Line Structure on an Aluminum Surface and the Nanoscale Patterning on the Nanoscale Structure using Highly-Functional Molecules**, ***Y. Watanabe***, *H. Kato, S. Takemura, H. Watanabe, K. Hayakawa, S. Kimura, D. Okumura, T. Sugiyama, T. Hiramatsu, N. Nanba, O. Nishikawa*, Kanto Gakuin University, Japan, *M. Taniguchi*, Kanazawa Institute of Technology, Japan

The surface of an Al plate was treated with a combination of chemical and electrochemical processes. Chemical treatment with acetone and successive electrochemical process were performed on the aluminum surface. Dynamic force microscopy (DFM) measurements after the chemical treatment demonstrated that a fibril-like structure with random widths in the same orientation was initially formed. The successive electrochemical process made the initial fiber-like structure more ordered and finer. The anodization successfully created a nanoscale highly-oriented line structure on an Al surface. The distance between the oriented lines was estimated as 30-40 nm. Furthermore, the present work intended to make an organic-inorganic nanoscale pattern using this nanoscale structure. Copper phthalocyanine (CuPc), fullerene C60, and polyaniline were selected in fabrication of functional nanoscale patterning. CuPc and C60 molecules were deposited on the highly-oriented line-structure on an aluminum surface. A toluene droplet containing CuPc molecules was cast on the Al plate and extended on the surface. CuPc deposition on the Al surface was made by evaporation of toluene. Cross section analysis of the DFM measurements clarified that each row line was filled with CuPc molecules because the line structure was clearly observed after the deposition. The depth of the row line became shallow and in some area the row width became narrower after the CuPc deposition. X-ray photoemission spectroscopy (XPS) measurements clarified that N 1s and Cu 2p lines appeared, which also supports the CuPc deposition on the nanoscale structure creating a nanoscale organic line pattern. The spectral profile difference of Al 2p pre- and after CuPc deposition suggested the molecular-surface interaction. Furthermore, the fabrication of a polyaniline nanowire along the row channel of the highly-oriented line structure was performed. A droplet of HCl solution containing aniline molecules was cast and extended on the nano-structured Al plate. Successively, a droplet containing APS was put and extended on the surface. DFM and XPS clarified that aniline molecules were polymerized in the channel. X-ray photoemission spectroscopy (XPS) and Fourier transform spectroscopy measurements supported the polymerization of the nanowire. This work was supported by High-Tech Research Center Project aided by MEXT.

**NM-ThP5 Fabrication and Photoluminescent Properties of Nanostructured Al Surfaces Topped by Polythiophene Film and Copper Phthalocyanine**, *H. Kato,* ***S. Takemura****, A. Ishii, Y. Takarai, H. Kobe, Y. Watanabe, T. Hiramatsu, N. Nanba*, Kanto Gakuin University, Japan

Nanostructures such as linked-crater structure and highly-oriented line structure were fabricated on an Al surface by combination process of chemical and electrochemical treatments. Conducting polymer polythiophene nanofilm growth on the nanostructured Al surface was conducted by an electrochemical synthetic method. Copper phthalocyanine (CuPc) doping in the nanofilm was conducted by a diffusion method. Photoluminescenct properties of the nanostructured Al surfaces and the surfaces topped by the nanofilm and CuPc were investigated. A nanoscale linked crater structure was fabricated on an Al surface by treatment with Semi Clean in order to create crater-shaped erosion on the surface as an initial structure. The successive electrochemical anodization in H2SO4 solution created a nanoscale finer linked-crater structure on the surface. The crater size was estimated as 80-150 nm in diameter. Dynamic force microscopy (DFM) measurements clarified that mall pores with 9 nm in diameter were created in each crater. Regarding the highly-oriented line structure, the anodization process applied to the original fiber-like surface structure on the Al plate. The anodization fabricated the finer line structure on the Al surface. The line distance was estimated as 40 nm. In the case of polythiophene film growth on the linked-crater structure, nanofilm was grown along the crater structure and the secondary structure remained demonstrated by DFM. Photoluminescence measurements on the linked-crater structure showed that five emission peaks appeared while no emission peaks were observed in the case of the original Al surface. Photoluminescence measurements on the polythiophene nanofilm on the linked-crater structure showed that the five emission peaks clearly appeared. The emission wavelengths were shifted. Furthermore, the photoluminescence measurement on the nanofilm doped with CuPc showed that the five emission peaks were enhanced. The photoluminescence measurements clarified that the nanostructured Al surface and the surface topped by nanofilm and CuPc molecules showed the characteristic emission properties for creation of functional hybrid materials. This work was supported by High-Tech Research Center Project aided by MEXT.

**NM-ThP6 Synthesis of Various Shaped Pt and FePt Nanoparticles**, ***N. Shukla****, M.M. Nigra, M. Bartel, T. Nuhfer, A.J. Gellman*, Carnegie Mellon University

We report the synthesis and self-assembly of controlled shapes and sizes of Pt nanoparticles using a high pressure synthesis technique. Our work suggests that solvent plays an important role in tailoring the shapes of Pt nanoparticles. Solvents can impact the synthesis because their boiling points dictate reaction trend and they also play a role as surfactants. Using various types of solvents under high pressure we have been able to synthesize Pt spheres, nanocubes and hexagons. 3D shapes of these nanoparticles are characterized using angle resolved high resolution TEM imaging. In addition, we report one step synthesis of core shell structures of cubic Pt nanoparticles. In this synthesis cubic Pt nanoparticles are the core and hexagonally shaped iron oxide/Fe is the shell. The most interesting part of this synthesis is that the shape of the core particles and shell is different. In most cases the core shells are either spherical or they acquire the shape of the nanoparticles. In this work we have achieved formation of cubic Pt nanoparticles with well hexagonal shaped iron oxide. These types of multiphase nanoparticles can have interesting applications in catalysis

**NM-ThP7 Analytical Model for Geometrical Characteristics Control of Laser Sintered Surfaces**, ***Y. Ioannou****, K. Polychronopoulou, C.C. Doumanidis*, University of Cyprus

Selective laser sintering (SLS) is an additive rapid manufacturing technique where high-power laser is used to fuse small particles into a specified 3-dimensional geometry. The goal of this work was to develop an analytical model for the SLS manufacturing processes, in order to control the geometrical characteristics of the sintered areas when iron/copper (Fe/Cu) powder alloy is used on a flat substrate. Powder particles are subject to melting by the laser energy and form a liquid globule, which solidifies as the laser beam spot moves on the substrate. The model is based on a system of lumped energy and mass balances, and the temperature field is computed via Green's function formulations by convolution of impulsive heat inputs at specific times and locations. The Green's function is dependent on the material conductive properties, substrate geometry, and boundary conditions. In considering the generated surface tensions due to powder melting, an approximation of the sintered area geometry after solidification of the material is performed via fluid dynamic equilibrium theory. Independent process parameters considered to govern the intensity of energy delivered to the powder material include laser power, beam spot size, beam velocity, hatch spacing and scan line length. Computational simulations are calibrated via and validated against experimentally fabricated SLS samples with simple deposition geometries.

**NM-ThP8 Low Damage Etching of $Ge_2Sb_2Te_5$ by using Halogen-Based Neutral Beams**, ***S.-K. Kang***, Sungkyun Advanced Institute of Nano Technology (SAINT), Korea, *B.J. Park, S.W. Kim, T.H. Min*, Sungkyunkwan University, Korea, *G.Y. Yeom*, Sungkyun Advanced Institute of Nano Technology (SAINT), Korea

Phase-change random access memory (PRAM) has made a prominent progress in memory performance and has brought a bright prospect for the next generation nonvolatile memory technologies due to its excellent advantages. One of the chalcogenide-based phase-change materials that have been paid attention for nanoscale nonvolatile memories is $Ge_2Sb_2Te_5$ (GST) which has advantageous properties such as high-speed phase transformation and high degree of read-write cyclability without any compositional change between different phases. Ge-Sb-Te based materials are known to be form halogenations easily and apt to be damaged when exposed to plasma in the etch process. In this work, we present X-ray photoelectron spectroscopy (XPS) data obtained from the surface of blank GST and etched GST features after etching in the halogen inductively coupled plasmas (ICP) such as $CF_4$, $Cl_2$ and HBr to investigate the extent of halogenation damage. And we also investigated surface damage of the GST etched by halogen-based neutral beam to compare with ICP process. Recently, the neutral beam etching (NBE) method is used by several researchers to avoid the charge-related damage. The damage related to charging can be eliminated because, compared to the conventional reactive ion etching, no ions participate in the etch process. Our neutral beam was formed using a low angle forward reflection of a parallel ion beam obtained by an ion gun. The XPS compositional depth profiling for the blank GST and the topological XPS analysis for the patterned GST were investigated after etching in the ICP and the NBE system to prove less damage process condition. In the etching of GST in halogen-based ICP and NBE system, the spectra of Ge, Sb and Te are shifted to higher binding energy region with different extents for different halogen-based plasmas. It indicates that GST film received different extent of damage for the halogen-based plasmas.

Significantly, we could observe the less changes of GST-degradation when the NBE was applied to etch the GST.

**NM-ThP9 Templated Self-Assembling Conducting Polymers as a Substrate for Nanoscale Design**, ***M.V. Lee***, *J.P. Hill, K. Ariga*, National Institute for Materials Science, Japan

Various strategies are being utilized to revolutionize nanoscale fabrication. A method based on a series of novel conductive polymers is demonstrated. Several functional groups can be incorporated into structures produced to affect both self-assembly and properties of the resulting polymer structures. Three dimensional structures for sensing and biological applications are envisioned.

**NM-ThP10 Plasma Treatment of PE Powder - From Laboratory Experiments to Production Plant**, ***P. Spatenka***, *J. Hladik*, Technical University of Liberec, Czech Republic, *J. Pichal*, Czech Technical University of Prague

Plasma modification of powder has recently attracted much interest because of new perspectives of the interfacial properties supervision. Plasma modified powder was used as a filler for composite materials or for production of components using roto-molding technique. Parts sintered from the plasma modified polyethylene powder preserved high surface tension, which allowed e.g. direct painting or adhesive bonding without any additional pretreatment. Plasma modification also significantly enhanced adhesion of the polymer to the substrate. Various methods for powder treatment have been reported for low-pressure plasma treatment of powder including fluidized bed or reactors with mechanical stirring. Based on laboratory experiments and analysis of various treatment methods we proposed a concept for industrial scale production of plasma-modified powder. The principle of the industrial-scale reactor will be presented. Production capacity and cost estimation will be also presented. Partial support of the projects KAN101120701 and MSM 4674788501 and GACR 106/08/1665 is greatly acknowledged.

## Plasma Science and Technology
## Room: Hall D - Session PS-ThP

## Plasma Science Poster Session

**PS-ThP1 Time-Modulated Etching in a Dual-Frequency Capacitively Coupled Fluorocarbon Plasma**, ***S. Jeong***, *D. Sung, K. Kim, A. Ushakov, M. Park, S. Cho, S. Kim, H. Park*, SAMSUNG ELECTRONICS, South Korea

Time-modulated etching process in a dual-frequency capacitively coupled fluorocarbon plasma has been investigated. In the pulsed-mode, etching rate non-uniformity decreased compared to the continuous-mode. The non-uniformity further decreased with lowering duty ratio. In addition, we find that more complex dissociation pattern in time-modulated fluorocarbon plasma than in continuous-wave driven plasma. Difference in the number of negative ions for the two different modes has been observed. We also discuss the relationship between the pulsed-mode process parameters and oxide-to-PR selectivities.

**PS-ThP2 In-situ Plasma Diagnostics Study of a Commercial High Power Hollow Cathode Magnetron (HCM) Deposition Tool**, ***R. Raju***, *L. Meng, H. Shin, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The development of special plasma diagnostic techniques is required to characterize the plasmas used in physical vapor deposition (PVD) and plasma enhanced chemical vapor deposition (PECVD) commercial tools because of the intense deposition environment, non-standard geometry, and non-standard frequencies. A commercial 200mm INOVA high power (36 kW) HCM deposition tool with computer controlled system was set-up and used as a realistic PVD test bed for designing and testing the new plasma diagnostics techniques. A 3-D scanning RF compensated Langmuir probe was designed, constructed and used to get spatial information of plasma temperature and density in the HCM tool at various input power (0-15 kW), pressure (10-70 mTorr) ranges. Measured electron temperature values are in the range of 1-3 eV and the electron density is between $6\times10^{10}$ to $2\times10^{12}$ $cm^{-3}$. While operating the tool, deposition of metal on the tungsten probe tip and the insulator probe body was observed. In order to sputter away the deposited material from the tip of the probe a self-cleaning in-situ plasma cup was designed. The plasma cup has a side cleaning station so that RF compensated Langmuir probe can be moved into it, cleaned and return to its original condition without being withdrawn from the system. We observed a considerable variation in electron temperature and density values after the probe was exposed in a 2 kW metal plasma for about 10 minutes. After cleaning the probe tip for about 8 minutes we observed a recovery of electron temperature to the initial value, however the measured electron density was not recovered. Further results revealed the importance of other effects such as probe temperature, temperature of the tool and the probe surface condition. The conductivity of the probe body surface decreases with an increase in deposition time. Hence it is necessary to clean the probe body as well as the probe tip to get more reliable plasma parameter values. A new method to clean the probe body in-situ has been implemented and results will be presented. Further experiments have been conducted to find the deposition rates and ionization fraction of the incident metal atom species employing a quartz crystal microbalance combined with electrostatic filters. A full 3-D scan of parameters is presented.

Acknowledgement: This work was supported by an SRC (Semiconductor Research Corporation) contract with Novellus custom SRC funding.

**PS-ThP3 Optical and Electrical Diagnostics of an rf-Capacitively Coupled Plasma**, ***H.W. Chang***, *C.C. Hsu*, National Taiwan University

Diagnostic studies of a low pressure rf capacitively coupled plasma in mixtures of Ar and $O_2$ were performed. This home-made plasma system has a cylindrical chamber with upper and lower annular electrodes; the electrode height can be adjusted. A voltage and a current probe were used to monitor the voltage and the current waveforms on the powered electrode with the focus of investigating the significance of the harmonics for plasma diagnostics. The amplitude, phase shift, and up-to-the 6th-harmonics of the voltage and current waveforms were recorded. The optical emission of the plasma was monitored using an optical emission spectrometer. It is found in this work that the 3rd and 4th harmonics become more prominent in Ar-rich conditions and the waveform shows a significant distortion from the 13.56 MHz sinusoid. Upon changing the electrode positions, the current and voltage waveform amplitude as well as the optical emission intensities of multiple peaks show variations below 20%. The 3rd and 4th harmonics in the current waveforms show up-to-50% variations throughout the conditions investigated. This suggests that the harmonic is a more sensitive measure for plasma monitoring. The correlation between operation conditions and diagnostic measurements will be established. The implication of the waveform harmonics to plasma processes will also be discussed.

**PS-ThP4 Characterization of Dual Frequency Capacitively-Coupled Oxygen Plasmas by Trace Rare Gases–optical Emission Spectroscopy (TRG-OES)**, ***Z. Chen***, *V.M. Donnelly, D.J. Economou*, University of Houston, *L. Chen, M. Funk, R. Sundararajan*, Tokyo Electron America, Inc.

Oxygen-containing plasmas are widely used for etching of fine features in microelectronics manufacturing. Dual-frequency capacitively-coupled reactors offer some advantages over inductive plasmas. The determination of the neutral species density and electron temperature ($T_e$) as a function of radio frequency (RF) power(s) and pressure are important in the understanding and optimization of the plasma etching processes in these systems. In this study, trace rare gases–optical emission spectroscopy (TRG–OES) was used to measure $T_e$, in a dual frequency capacitively-coupled oxygen plasma sustained by a high frequency (60 MHz) “source” upper electrode, and a 13.56 MHz voltage applied to the wafer-supporting lower electrode. TRG-OES is a nonintrusive method for determining plasma electron temperature and, under some conditions, electron energy distributions. The method is based on a comparison of atomic emission intensities from trace amounts of rare gases (a mixture of He, Ne, Ar, Kr, and Xe) added to the plasma, with intensities calculated from a model. In the present experiments, a small amount (5%) of a mixture containing 40% Ne, 20% Ar, 20% Kr and 20% Xe was added to the $O_2$ feed gas. $T_e$ was measured across the plasma at a height of 5 mm above the lower electrode as a function of pressure (2-200 mTorr) at different applied RF powers. Oxygen atom densities were estimated by O-atom optical emission (844.6 nm), and rare gas actinometry (Ar, 750.4 nm). Results illustrated that $T_e$ in an $O_2$ plasma with 1000 W upper power and no lower electrode power varies inversely with pressure, from 6.8 eV at 2 mTorr to 3.5 eV at 200 mTorr. As power was increasingly applied to the lower electrode, $T_e$ at low pressure (e.g. 2 mTorr) hardly changed while, at higher pressures, $T_e$ increased to the point that at 500 W lower electrode power, $T_e$ was nearly independent of pressure. Percent dissociations derived from O-atom densities were quite low (<5%), even at the highest upper electrode power.

**PS-ThP5 Synthesis of Single-Walled Carbon Nanotubes by Oxygen-Assisted Plasma Enhanced Chemical Vapor Deposition**, ***S.W. Huang***, *C.H. Hsiao, K.-C. Leou, C.-H. Tsai*, National Tsing Hua University, Taiwan

Single-walled carbon nanotubes (SWNTs) have attracted a great deal of attention recently due to their unique physical properties and a wide range of potential applications, in particular, field effect transistors (FET) and nano-photonic devices. It is highly desirable to develop a method compatible with standard semiconductor microfabrication processes for direct synthesis of high quality SWNTs. In this work, we demonstrated a low temperature growth process of SWNTs on silicon substrates by inductively coupled plasma chemical vapor deposition (ICP-CVD) method with $CH_4/H_2$ gas mixture as base processing gases. A unique $Ni/Al/SiO_2$ nanocatalysts/support system has also been developed to allow the growth of high quality SWNTs. To further improve the crystalline structure of SWNTs, oxygen was added to the processing gas mixture to remove amorphous carbons during the growth process. Both the scanning electron microscopy and micro-Raman spectra were employed for characterizations of the SWNTs. The SWNTs were successfully synthesized at a temperature as low as 600°C. Parametric experiments were conducted to optimize the $O_2$ fraction in the gas mixture. Experimental results show that a low fraction of Oxygen not only increases the growth rate of SWNTs but also improve the quality of the tubes. The SWNTs are damaged, however, if the fraction of oxygen is too high.

**PS-ThP6 Characterization of Platinum Catalyst Supported on Carbon Nanoballs Prepared by Solution Plasma Processing,** ***Y. Ichino****, K. Mitamura, N. Saito, O. Takai*, Nagoya University, Japan

Nonequilibrium plasma in aqueous solution, which is solution plasma (SP), is expected as a frontier of plasma nanomaterials processing. The SP processing can realize rapid synthesis at low temperature compared to the conventional methods such as chemical synthesis in solution and plasma processing in gas. We had successfully synthesized Au, Pt and FePt nanoparticles by SP processing. On the other hand, carbon nanoball (CNB) is one of carbon nanomaterial such as carbon nanotube (CNT) and fullerene. The CNB is expected as an electrode material for fuel cells. We already have been successful to synthesis well-defined CNBs. In order to improve the energy-conversion efficiency in fuel cells, Pt nanoparticles must be mounted on CNBs in the high density. In this study, we aim to prepare Pt nanoparticles in the high density supported on CNB (Pt/CNB) by using SP processing and to characterize the properties as the electrode for fuel cells. Carbon nanoball was prepared by thermal CVD process. Ethylene was used as a raw material. Argon and hydrogen ware used as carrier gases. Solution plasma was generated by a pulsed power supply. Tungsten wire coated with alumina was used as the electrodes. 1.44 mM $H_2PtCl_6$ solution was added to 50 mg CNB, and polyvinylpyrrolidone (PVP) or sodium dodecyl sulfate (SDS) as a protective agent. After the discharge, the obtained Pt/CNBs were characterized by a scanning transmission electron microscope (STEM), energy dispersive X-ray spectroscopy (EDS) inductively-coupled plasma optical emission spectrometry (ICP-OES). The catalytic properties of Pt/CNB was evaluated by cyclic voltammetry (CV). Color of the solution changed from yellow to dark brown as synthesis time. This change indicates the decrease of $H_2PtCl_6$ complex in the solution and the improvement of dispersibility of CNB. Moreover, STEM images and elemental mapping images show the Pt nanoparticles supported on CNB. A catalytic activity of the obtained Pt/CNB was shown to be higher than the Pt/CNB prepared by conventional method since the adsorption wave of hydrogen was observed from CV. The activity was varied by the amount of supported Pt nanoparticles, which depended on SP processing conditions.

**PS-ThP7 Effect of Dissolved Gases and Ions onto Solution Plasma Fields,** ***N. Fujikawa****, N. Saito, O. Takai*, Nagoya University, Japan

Solution Plasma (SP) is defined as a nonequilibrium discharge phenomenon in liquid solution. The higher reaction rate is expected since it supplies UV light, electrons, and radicals to liquid phase. SP processing is one of attractive reaction field for nano materials synthesis. However, there are few reports on solution plasma processing, in particular, fundamental research. We had been successful to fabricate various nanoparticles such as Au, Pt, FePt, $In_2O_3$ by SP processing. The reaction mechanism in the solution plasma has not been understood in detail. Reduction must be mainly occurred on these syntheses. However, oxygen and oxygen radical also be produced in the solution plasma. Why does not oxidation proceed? There are many other questions in SP processing. In this study, we aimed to investigate influences of dissolved substance, eg. $O_2$, ions on the reactive species in the solution plasma. A pulsed power supply was utilized to generate plasma. Needle-shaped tungsten (diameter: 1 mm) was utilized as an electrode. Voltage between electrodes, pulse width and frequency were 2400V, 2μs and 15kHz, respectively. Optical emission spectra were measured with a emission spectrophotometer. Ar or $O_2$ gases were introduced into the solution in order to vary the amount of dissolved oxygen. Discharge time was 30min. and solution temperature was varied from 10 to 30$^{o}$C. Moreover, several kinds of chlorides were added into liquid solution in order to observed influences of ions. Peaks attributed to $H_\alpha$, $H_\beta$, $H_\gamma$ and O were observed in optical emission spectra. The presence originated from decomposition of water. The each intensity is almost constant although the flow rates of $O_2$ and Ar gases varied. From this, dissolved oxygen did not have a great effect on plasma state. On the other hand, peaks attributed to cation produced from chlorides were observed although peaks of chlorine were not observed. These differences would be discussed from the viewpoint of mobility in the solution, molecular weight, molecular or ion radius, and the reactivity of activated species.

**PS-ThP8 Organic Compounds Synthesized by Short-Pulsed Discharge in Aqueous Solution,** ***T. Mori****, K. Mitamura, N. Saito, O. Takai*, Nagoya University, Japan

Some scientists had attempted amino-acid synthesis in order to represent origin of livings. For example, S.L.Miller obtained amino-acid after generating cyanide and aldehyde from discharged mixture gas, which consisted of $NH_3$, $CH_4$, $H_2$ and $H_2O$. This gas is main composition in primitive atmosphere in ancient times. Recently, we had been successful to generate solution plasma, which is one of pulsed discharge phenomenon in the solution. This is nonequilibrium plasma in solution. Thus, we can form cold plasma in the solution. Solution plasma supply many amount of radicals, ions and electrons, and intensive ultraviolet even at room temperature. Such state might be found on the earth, in particular, near seawater surface. In this study, we attempted to synthesize amino-acid by using the solution plasma in C-H-O-N solution system. As first experiments, organic synthesis with solution plasma was conducted in methanol and water system. Solution plasma was generated by using a short-pulsed power supply. After discharge, the ninhydrin solution was added to the obtained solution in order to confirm the formation of amino-acid through ninhydrin reaction. When amino-acid is produced, the color of the solution changes into Ruhemann's purple. Moreover the product in the solution was analyzed by nuclear magnetic resonance (NMR). While the ratio of methanol to water was varied, the amount of products and their species were investigated in detail. Solution plasma was generated in solution consisting of ethanol and water. Formation of acetaldehyde in the solution was confirmed by silver-mirror reaction and NMR analysis. Formation of $CH_4$, $H_2$ and $O_2$ gases was also confirmed by gas chromatography. The gases might be produced via several recombination reaction between radicals in the solution plasma. Additionally, while the ratio of ethanol to water was varied, the generation amount of $CH_4$ and $H_2$ changed drastically. The variation of ratio has a great influence on excited state and the reaction in the solution plasma. The productants synthesized in other solutions were discussed as same manner.

**PS-ThP9 Excited Species by Shorter-Pulsed Electrical Discharges in Aqueous Solutions: Effect of Electrodes with Low Work Function,** ***C. Miron****, M.A. Bratescu, N. Saito, O. Takai*, Nagoya University, Japan

Pulsed electrical discharges in water have shown to produce hydrogen, ozone, oxygen, hydroxyl radicals and other chemically active species, making these techniques useful for several applications, such as water purification, nanoparticles synthesis. The electrical discharges in liquids were realized using different types of electrodes, such as copper, tungsten, stainless steel. During the experimental work many difficulties have been encountered due to the sparks and electrodes erosion process. Electrodes of high melting point, corrosion-resistant and high stability are required in realizing the electrical discharges in liquids. The objective of the present work is to investigate the optical properties of a pulsed glow discharge in ultrapure water between two electrodes with low work function, such as lanthanum hexaboride and tungsten. The effect of the electrode material on some physicochemical processes generated in solution plasma was realized by using time-resolved optical spectroscopy technique. Lanthanum hexaboride (LaB6) cathode has high stability and a very low work function (2.5 eV) in high vacuum, which changes when temperature is increased. Also is an excellent electron emitter material due to the oxygen adsorption on the lanthanum sites. The lifetime of these cathodes is 10 – 15 times longer than that of the tungsten cathodes. The behavior of the plasma and some properties of the LaB6 and tungsten electrodes, their effects on the time evolution of the reactive species generated in the electrical discharges in water were investigated in the present work. Time-resolved optical spectroscopy of the reactive species generated in the plasma showed a different evolution in time, depending on the electrode material, the life time of the excited species, and pulse polarity of the applied pulsed voltage. The electron temperature in the plasma was very low when LaB6 electrodes were used in the process, compared to the electron temperature obtained in the atmospheric pressure air plasmas. The low value of the electron temperature explains the broad band spectrum of the molecular species acquired in the electrical discharges generated in ultrapure water.

**PS-ThP10 Effects of Vacuum-Ultraviolet Radiation on the Plasma-Induced Charging of Patterned-Dielectric Materials,** ***G.S. Upadhyaya****, J.L. Shohet*, University of Wisconsin-Madison

In this work, the effects of vacuum-ultraviolet (VUV) radiation on plasma-induced charging of patterned-dielectric structures are investigated. Experimental results show that supplemental-VUV radiation exposure of patterned dielectrics is beneficial in minimizing the plasma-induced charge on patterned-dielectric structures. The results of this work indicate that exposure of patterned-dielectric materials to VUV radiation during plasma processing can be useful in reducing or eliminating structural and electrical damage caused to patterned dielectrics by electron shading. Investigation of the effects of VUV radiation on the plasma charging of dielectrics was accomplished by evaluating the response of unpatterned, plasma-charged, oxide-coated samples exposed to monochromatic-synchrotron-VUV radiation at the University of Wisconsin-Synchrotron Radiation Center. VUV exposure of unpatterned SiO2/Si wafers indicated that photon energies less than or equal to 11 eV are beneficial in depleting the plasma-induced charge. The radiation-response experiments were subsequently extended to include patterned-dielectric wafers. Specialized, patterned-test structures with different aspect ratios (depth/width of a pit) were charged in a DC plasma and subsequently exposed to monochromatic-synchrotron-VUV radiation. Surface-potential measurements revealed significant charge depletion for photon energies in the range from 8-11 eV thereby indicating the beneficial effect of VUV radiation during plasma processing of patterned dielectrics. In addition, it was observed that the number of photons required to deplete charge in patterned dielectrics increases with the increasing aspect ratio of the pits in the patterned wafer. The experimental results are explained with equivalent-circuit models which suggest that electron photoinjection from the Si substrate as well as oxide surface conductivity play an important role in depleting the plasma-induced charge on the patterned-dielectric materials. Thus, we conclude that plasma-charging-induced damage in patterned-dielectric materials can be minimized by supplemental VUV exposure of the wafers during plasma processing.

Work supported by NSF under Grant DMR-0306582 and in part by the Semiconductor Research Corporation under Contract 2008-KJ-1781. The UW Synchrotron is a National Facility supported by NSF under Grant DMR-0084402. *G.S. Upadhyaya present address: Lam Research Corp., Fremont CA. .

**PS-ThP11 How Far Should Be for Being Remote Plasma?**, ***Y. Kim***, *W.K. Yang, J.H. Joo*, Kunsan National University, Korea

Remote plasma has been used in PEALD to reduce adsorbed precursor into a compound layer like $HfO_2$. The demanding role of plasma is a supplier of radicals not ions which might induce charge damage to devices. We focused the effects of plasma in two aspects; ion transport and thermal energy transfer to the wafer which have been underestimated in previous works. Advanced Energy's Remote Plasma Source is installed 300mm above a wafer and operated at a few to hundreds of mTorr range, within 1.5kW. Plasma was well localized within the quartz chamber region at high pressure regime due to reduced mobility of charged particles. At 10mTorr, plasma was spread to all over the chamber. Measured surface temperatures at four points from the wafer showed 50, 70, 150, and 600°C within a minute from ignition of Ar ICP(~2MHz, 500W). Temperature rise at the wafer surface could be from three mechanisms: ion kinetic energy, ion and meta-stable recombination heat release. We developed a 2D and 3D fluid based model using CFD-ACE+ to investigate heat transfer from plasma source including chamber outside cooling by air.

**PS-ThP12 Real Time Feedback Control of Plasma Density by using a Floating Probe in Inductively Coupled Plasmas**, ***S.H. Jang***, *M.H. Lee, C.W. Chung*, Hanyang University, Republic of Korea

A real time feedback control of plasma density to apply processing plasmas was carried out experimentally in inductively coupled plasma (ICP). The plasma density control can contribute good processing performance because etched and deposition rate are generally a function of the plasma density, and it influences other processing parameters such as the number of radicals, uniformity, processing time etc. In this study, the plasma density was measured by a floating probe which can measure the plasma density in real time without plasma perturbation installed as a sensor on a chamber wall, and the measured information was fed back to actuator to influence the plasma density. This plasma control system allowed the plasma density to reach and keep the desired densities below 0.1% of the state error. To describe External disturbances, the pressure of the chamber was dropped from 10 mTorr to 5 mTorr by using a molecular flow controller. At the pressure disturbance, the density decreases, and recovers with 1.5% of the maximum error and 10 s of the settling time. In the comparison of active and inactive control with pressure disturbance, the Maximum state errors were 1.5% and 40% respectively.

**PS-ThP13 Time Resolved Measurements of the Electron Density with a Cutoff Probe in a Pulsed Plasma**, ***J.-H. Kim***, *S.J. You*, Korea Research Institute of Standards and Science, *B.-K. Na*, Korea Advanced Institute of Science and Technology, *D.-J. Seong, Y.-H. Shin*, Korea Research Institute of Standards and Science

In pulse-modulated capacitively coupled plasmas generated in Ar/CF4 mixtures, time variations of the electron density were measured with a cutoff probe. For measuring the cutoff frequency, a microwave is introduced through a radiating antenna to the plasma, and the transmitted wave is detected on a receiving antenna connected to a port of an oscilloscope. From the transmission spectrum we obtained the wave cutoff frequency, which could directly give the electron density. To measure the time variation of cutoff frequency, we scanned the transmitted signal with time for a fixed frequency, which was done for next fixed frequency and so on. Thus, we accumulated the time variations of the transmitted signal data for each different frequency and transposed the data array. Therefore, we obtained the time variation of the cutoff frequency. We investigated the decay time of the electron density for different pressures, repetition frequencies of the pulse modulation, and duty ratios.

## Advanced Surface Engineering
## Room: Hall D - Session SE-ThP

## Advanced Surface Engineering Poster Session

**SE-ThP1 Investigation of Polarization Conversion Effect in Obliquely Deposited SiOx and $As_2S_3$ Films**, ***M.V. Sopinskyy***, *I.Z. Indutnyy, V.I. Mynko, P.E. Shepeliavyi*, V Lashkaryov Institute of Semiconductor Physics, NASU, Ukraine

Polarization conversion effect have been studied to find out anisotropy in the obliquely deposited SiOx and As2S3 films. The films were obtained by thermal evaporation and oblique deposition of SiO and As2S3 onto polished Si and silica substrates. During deposition the substrates were oriented at the angles β between the normal to the substrate surface and the direction to the evaporator. The polarization conversion is an interesting phenomenon which causes the fraction of p(s)-polarized light incident on an anisotropic thin film be reflected as s(p)-polarized light.[1] The optical anisotropy of the obliquely deposited SiOx and As2S3 films was detected using the data on the polarization conversion of the electric vector caused by the passage of polarized light through the film. For this purpose the light beam with the electric vector linearly polarized in the direction perpendicular to the plane of incidence (the s-polarized light beam) was projected on the samples and the ellipsometer table was rotated around the normal to the sample surface (rotation angle α = 0°-360°). The angular rotation of analyzer (θ) was measured by means of the ellipsometer with a sensitivity of 0.02°. Normally deposited SiOx and As2S3 films don't show any in-plane anisotropy. For As2S3 films deposited at β=75° and SiOx films deposited at β=60° there are observed θ(α) dependencies with the period of 180° (symmetrical, or assymetrical). In this case, principal axes of high-frequency dielectric constant tensor εik for those films are mutual perpendicular, and two of them lie in the plane parallel to film substrate (one is parallel, and another perpendicular to the direction of the projection of the vapor-beam's direction on the substrate surface). The third principal axis of εik is perpendicular to the substrate surface or is slightly inclined to the perpendicular. For SiOx films deposited at β=75° θ(α)-dependencies have 360°period value. In this case the third principal axis of εik is inclined toward the substrate surface. It directly shows that obliquely inclined columns are formed in such films. Thus, investigation of polarization conversion effect is simple, nondestructive and useful method to distinguish the type of in-plane and out-of-plane structural anisotropy of obliquely deposited films.

[1] R. M. A. Azzam and N. M. Bashara, (1986). Ellipsometry and Polarized Light (Amsterdam: North-Holland).

**SE-ThP2 Influence of Oblique Incidence on the Properties of Ion Beam Sputtered Chromium and SmCo Films**, *B. Ramamoorthy*, Indian Institute of Science, *A. Raju*, Honeywell Technology Solutions Lab, ***S. Mohan***, Indian Institute of Science

Ion Beam Sputter Deposition (IBSD) technique with its unique characteristics like lower operating pressure, well collimated mono energetic beam, independent control over the energy and flux is considered superior over the conventional sputtering techniques in processing thin films with tailored properties. In addition to the above features, the energy of the sputtered species is also relatively higher in IBSD. The spatial and angular distribution of the sputtered species here, also could be controlled by controlling the incident angle of ions over the target. This ability to fine control the energy of the sputtered species has been well utlized in depositing high density optical films. This energy imparting kinetics also forms the basis for the commonly used ion assisted deposition. Though the energy advantages have been well utilized, the angular distribution has not been explored much. In this work, we explore the advantages of angular distribution of the sputtered species, in modifying the properties of Cr and SmCo films. In the IBSD system used in the present study , ions were incident over the targets at an angle of $45^o$ degrees and substrates were placed at angles $10^o$, $20^o$ and $30^o$ measured from the target normal. The substrates were heated to $600^o$ C. Chromium and SmCo films were deposited sequentially without breaking the vaccum. The deposited films were studied for their composition, structure and their magnetic properties. The structural studies indicate different structural orientations with different substrate position. Self shadowing of the condensed atoms, higher mobility on the plane of the substrate during oblique incidence have been found to be responsible for the structural variations which otherwise would not have been possible with other process parameter combinations. The change in the structure has also been found to alter the magnetic properties of the films. The films deposited at normal incidence show a coercivity of 4kOe whereas the films deposited at an angle of $30^o$ show a coercivity of 6kOe. The increase in the coercivity has been attributed to the preferential orientation of SmCo films caused due to the oblique incidence. The results obtained will be discussed in detail from the context of oblique deposition.

### SE-ThP3 Characterizations of Polarization-Discriminatory Inverters Fabricated by Glancing Angle Deposition, *Y.J. Park*, *K.M.A. Sobahan*, *C.K. Hwangbo*, Inha University, Republic of Korea

Glancing angle deposition (GLAD) is a thin-film fabrication technique with controlled microstructures and provides advantages over conventional evaporation techniques. Based on physical vapor deposition, it employs an oblique-angle-deposition and substrate motion to allow nanometer-scale control of the structure in engineered thin-film materials. The films deposited in this technique show the optical anisotropy originating from the microstructures and the porosity of the films increase due to shadow effects. These controls can be utilized to engineer thin films for specific applications such as three-dimensional photonic crystals, gradient index optical filters, broadband antireflection coatings, and linear polarizer, etc. In this study, we investigate the optical and structural properties of linear and circular polarization-discriminatory inverters. Circular polarization-discriminatory handedness inverter is realized as a combination of half-wave plate and Bragg reflector and that of linear polarization inverter is realized as a combination of quarter-wave plate, Bragg reflector and quarter-wave plate. The zigzag microstructures of the quarter-wave plates as well as the half-wave plates and the helical structure of the Bragg reflector are fabricated by electron beam evaporation using GLAD technique and Ti@O@sub 2 material is used in this purpose. The physical thicknesses of the half and quarter-wave plates are calculated using their anisotropy. The polarization-discriminatory inverters show that the incident linear and circular polarized light becomes opposite linear and circular polarized lights with Bragg effect at output. The structural and surface morphology of this device are also investigated using scanning electron microscope (SEM).

### SE-ThP4 Influence of Substrate Temperature on Reactive-sputtered Tin-nitride Thin Films Prepared by Glancing Angle Deposition, *H. Tsuda*, *H. Takeuchi*, *Y. Inoue*, *O. Takai*, Nagoya University, Japan

1. Introduction Properties of tin-nitrogen compounds have not been recognized in detail. Tin-nitride was reported to exhibit a spinel structure ($Sn_3N_4$) at low temperature, while tin-nitride films deposited at high temperature showed a zinc blende (SnN) structure. As one of the properties of tin nitride, we found that amorphous tin-nitride (a-SnN) films prepared by reactive ion plating show an erectrochromic (EC) phenomenon, which is a reversible color change of materials induced by applying a burst of electrical charge. We have reported that the EC phenomenon occurs due to the change of surface adsorption at indium nitride film, so that the color-change efficiency is strongly influenced by surface area. Moreover, it is influenced by crystallinity. Therefore, both the expansion of surface area and the improvement of crystallinity are important. In this study, we aim to investigate the properties of reactive-sputtered tin-nitride thin film prepared by glancing angle deposition (GLAD). 2. Experimental procedure The tin-nitride films were prepared by using a conventional rf magnetron sputtering system. After evacuation of a deposition chamber under $1\times10^{-3}$ Pa, high-purity $N_2$ gas was introduced into the chamber up to 1 Pa. Then rf power (13.56MHz, 75W) was applied to a metallic tin target of 4N purity. The angle of a substrate holder against the sputtered tin flux was set at 0° and 85°. In-plane rotation condition of the substrate holder was controlled by a motor. We used both Si (100) single crystal wafers and glass plates as substrates. The substrate temperature was controlled by a halogen spot heater. Crystallinity and microstructure of the films was characterized by an X-ray diffractometer (XRD) and a scanning electron microscope (SEM). 3. Results In the case of non-heating substrates, we confirmed that both the samples deposited at 0° (sample A) and at 85° (sample B) have the spinel ($Sn_3N_4$) crystal phase. The cross-sectional surfaces of the sample A showed a dense columnar structure. EC characterization revealed that the sample A shows no EC phenomenon. On the other hand, the microstructure of the sample B is quite similar to the microvillus structure of small intestine, which consists of isolated nanocolumns. The sample B showed small EC phenomenon, which may due to the surface area much expanded than that of the sample A.

### SE-ThP5 Electrochromic Response of InN Thin Films with Microstructures Controlled by Glancing-angle Deposition, *H. Ishikawa*, *H. Takeuchi*, *Y. Inoue*, *O. Takai*, Nagoya University, Japan

1. Introduction Electrochromic (EC) materials change their colors reversibly by applying a burst of electrical charge. Indium nitride (InN) thin films also show EC phenomenon by applying electric potential in a solution. The mechanism of the EC phenomenon in InN is quite unique. We have found that the EC of InN is induced by alternation of surface adsorbates, which means that InN is suitable for high-response EC devices. We have improved the EC properties of InN films by introducing a microvillus-like isolated nanocolumnar structure prepared by glancing-angle deposition (GLAD) in order to expand the effective surface area. However, the microvillus-like structure includes so deep gaps that the EC response property is degraded. In this study, we deposit InN films which have large effective surface area with low-height columnar structure, and their EC response property is investigated. 2. Experimental procedure InN films were deposited on ITO-coated glass plates by using a reactive ion plating system. After evacuation of a deposition chamber, pure $N_2$ gas was fed into the chamber at a constant gas flow of 19.0 sccm. The total pressure was controlled from 1.0 to 7.0 Pa. In order to activate $N_2$ plasma, a 13.56 MHz RF power of 150 W was applied to a RF antenna in the chamber. The crucible for In was resistively-heated to evaporate In metal shots (6N) in the $N_2$ plasma. The substrate holder was rotated during deposition at the angle of 0° or 85° with respect to the vapor fluxes. The crystallinity of the deposited films was investigated by using an X-ray diffractometer (XRD). We investigated the EC properties of the films by using both a UV-Vis spectrophotometer and an EC response measuring unit which consist of a laser diode (650 nm) and a Si photodiode. 3. Results From the XRD profiles, we confirmed that any film deposited in this study has a wurtzite crystal structure. The films deposited without GLAD technique at the total pressure of 1.0 Pa (sample A) and 2.0 Pa (sample B) have a vertical columnar structure with the columnar radius and porosity dependent on the pressure. The EC response of the sample B is faster than that of the sample A. The film deposited with GLAD configuration at the substrate angle of 85° (sample C) has much higher porosity than the samples A and B. Therefore the EC amplitude of the sample C is improved, while the EC response of the sample C was almost same as that of the sample A.

### SE-ThP6 Hard Transparent Conducting Nb-doped Titania Films by Reactive Co-Sputtering, *K.H. Hung*, *H.C. Hsing*, *W.C. Hsu*, *M.S. Wong*, National Dong Hwa University, Taiwan

The outstanding properties of titania have made them useful for many applications including photocatalysis, gas sensors, dielectric thin-film capacitors and solar cells. However, researchers have not paid much attention to their transport properties and mechanical behaviors. We have produced a series of niobium-doped titania films by reactive co-sputtering titanium and niobium targets and by subsequent annealing the films in a hydrogen environment. The composition of the films was modulated by changing the niobium target power; consequently, niobium content of the films changed from 0 to 4.2 atomic percent. The characterization studies show that the annealed films are polycrystalline with anatase phase without accompanying other crystalline oxide phases. The results also demonstrate that the films possess high visible-light transparency as well as enhanced hardness and conductivity. For instance, the doped titania film of 2.8 at% Nb deposited at a substrate temperature of 350 °C and annealed at 600°C exhibits an average transmittance of 70% in visible light region and a high hardness up to 11.4 GPa. Moreover, the Hall measurements of the film reveal n-type semiconducting behavior for this film with a reduced resistivity of 9.2E-4 ohm-cm, a carrier density of 6.61E21 $cm^{-3}$ and a mobility of 1.0 $cm^2v^{-1}s^{-1}$.

### SE-ThP7 Effect of Water Pulsed Plasma on Electrode Surface, *N. Apetroaei*, *N. Saito*, *O. Takai*, Nagoya University, Japan

The aim of this paper is to contribute to a better understanding of the mechanisms, which conducted to the electrode surface modifications using the water plasma, and to correlate these experimental results with the results which we obtained from diagnosis of the plasma. The water pulsed plasma is non-equilibrium highly collisional plasma produced at rather high pressure by high voltage pulse applied to a special system of electrodes. Different electrode materials, shapes and configuration have pronounced effect on liquid discharge. In our case were used to form the electrodes, wire and rod of copper, tungsten, tantalum, molybdenum, nickel and stainless steel (SUS) with different diameter from 1mm up to 3mm for tip to tip electrode configuration and sheet of Cu and SUS for plan to plan and tip to plan electrode configuration. The high voltage power supply (4 kV) generates bipolar pulses in the range of 2 – 10μs and frequency in the range of 1 - 30 kHz. Modification of surface properties of a metallic electrode has been analyzed by contact angle measurement, scanning electron microscope (SEM) and X-ray photoelectron spectroscopy (XPS). Water plasma changes the electrode surface structure. There are few things which conduct to these changes. One is strong local heating and formation of hot spots at the electrode surface. Temperatures above the boiling point of the electrode material can de necessary depending on the work function of the metal. Another is discharge physical sputtering caused by the collision of energetic electrons or other heavy particles with electrode surface. Another is the chemical reaction between water plasma and electrode surface. Water plasma generates very active species such as: chemical aggressive atoms and radicals, charged particles-electron and ions, excited atoms and molecules. After solution plasma we observed that the proprieties (surface tension, adhesion work, roughness, oxidization) of electrode surface have changed, comparing to a new one unused to water plasma. Surface wettability is improved from contact angle measurements and SEM images show an increase of surface roughness.

**SE-ThP8 A Comparative Study on the Mechanical Properties and Thermal Stability of Cr-Zr-N and CrSi-Zr-N Coatings Synthesized by Closed Field Unbalanced Magnetron Sputtering,** ***G.S. Kim****, Y.S. Kim, S.M. Kim, S.Y. Lee, B.Y. Lee*, Korea Aerospace University

Recently, the synthesis of Cr-Zr-N coatings by adding an heterogeneous atom, Zr into CrN film was successfully made using a closed field unbalanced magnetron sputtering and these Cr-Zr-N coatings are reported to have not only much improved mechanical properties, but also a very low surface roughness with increasing Zr content. Especially, the average friction coefficient against $Al_2O_3$ counterpart ball of the $Cr_{1-x}Zr_xN$ (X=0.34) coating was measured to be approximately 0.17 at room temperature and this value is approximately 3.5 times lower than that of CrN film (approximately 0.6). However, investigations on the high temperature characteristics of the Cr-Zr-N coatings revealed their mechanical properties are severely deteriorated at 500 ℃ due to the surface oxidation and the decrease of hardness by means of the residual stress relaxation. In this work, to improve the high temperature mechanical properties of the Cr-Zr-N films, the CrSi-Zr-N coatings were synthesized from CrSi(Si=10 and 20 at.%) and Zr targets by a closed field unbalanced magnetron sputtering and their chemical composition, crystal structure, morphology and mechanical properties were characterized by glow discharge optical emission spectroscopy (GDOES), X-ray diffraction (XRD), scanning electron microscopy (SEM), atomic force microscopy (AFM) and nanoindenter. Also, the thermal stability of the CrSi-Zr-N coatings was evaluated by annealing the thin films at temperatures between 300 and 900 ℃ for 30min in air. The experimental results showed the CrSi-Zr-N coatings exhibit higher thermal stability and mechanical properties compared to those of Cr-Zr-N coating with increasing Si content. Detailed experimental results included wear test at 500 ℃ will be presented.

**SE-ThP9 A Comparative Study on the Thermal Stability of CrN, CrSiN and CrSiN/AlN Multilayer Coatings,** ***S.M. Kim****, G.S. Kim, S.Y. Lee, B.Y. Lee*, Korea Aerospace University

In this work, CrN, CrSiN and CrSiN/AlN multilayer coatings were synthesized from Cr, Al and CrSi (Si= 10 at. %) targets using a closed-field unbalanced magnetron sputtering system (CFUBMS). The coatings have been characterized by glow discharge optical emission spectroscopy (GDOES), X-ray diffractometry (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS) and nano-indentation. The maximum hardness of CrSiN/AlN multilayer coating with the bilayer period (@lamda@) of 3 nm was approximately 32 GPa, whereas CrN and CrSiN coatings exhibited the maximum hardness of 22 and 27 GPa, respectively. Thermal stability of CrN, CrSiN and CrSiN/AlN multilayer coatings was investigated with annealing treatment for 30 min in air in the temperature range of 600 to 800 °C. The XRD patterns showed that CrN and CrSiN coatings were severely oxidized at 700 °C. However, in the case of CrSiN/AlN multilayer coating, no detectable oxides were observed even at 800 °C. After annealing at 800 °C, the hardness of the CrSiN/AlN multilayer coating exhibited approximately as high as 29 GPa compared to the CrN and CrSiN coatings, which showed only 8 and 18 GPa, respectively. These results revealed that the thermal stability of the CrSiN/AlN multilayer coatings were much superior to that of the CrN and CrSiN coatings at elevated temperatures because the AlN films in the CrSiN/AlN multilayer coatings retard the oxygen diffusion into the coatings. The detailed experimental results will be presented.

**SE-ThP10 Investigation of Photocatalytic Activity of $TiO_2/WO_3$ Bilayered Thin Films with Various Amounts of Exposed $WO_3$ Surface,** *S. Biswas, M.F. Hossain, M. Shahjahan,* ***K. Takahashi****, T. Takahashi,* University of Toyama, Japan, *A. Fujishima*, Kanagawa Academy of Science and Technology, Japan

$TiO_2$ is the most widely used photocatalyst for effective decomposition of organic compounds in air and water. However, its technological application is limited by the need for an ultraviolet (UV) excitation source. One of the most promising methods to extend the light-absorbing property of $TiO_2$ and to enhance its photocatalytic efficiency is to couple $TiO_2$ with narrow-bandgap semiconductors, which act as a sensitizer. Tungsten oxide ($WO_3$) with band-gap 2.8 eV, is a promising candidate to be used as under-layer for $TiO_2$ photocatalysts. However, $WO_3$ should have some amount of uncovered surface so that it can act as a reducing agent. In this study, $WO_3$ films were deposited on glass substrates, using facing target dc reactive sputtering technique and the upper $TiO_2$ thin films were also deposited with the same technique using different masks to leave various amounts of $WO_3$-exposed surfaces: 0%, 30% and 80%. The crystallographic properties, surface structures and optical properties of $WO_3$ films were investigated in detail. The X-ray diffraction patterns show triclinic and anatase crystal structure for the $WO_3$ films and $TiO_2$ films, respectively. The optical and surface morphological properties of both $WO_3$ and $TiO_2$ layers have been studied using UV-visible spectrometer, field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). The photocatalytic activity was measured by the rate of photodecomposition of methanol in UV and visible light irradiation, evaluated by Fourier transform infrared spectrometer (FTIR). The results show that with the variation of $WO_3$ exposed area, photocatalytic activity of $WO_3$/ $TiO_2$ system varies significantly. It is revealed that, with the increase of $WO_3$-exposed surface photocatalytic activity increases initially, but it decreases with the further increase. The result has been tried to be explained on the basis of methanol-photodecomposition mechanism and the amount of relative exposed surface of $WO_3$ and $TiO_2$.

**SE-ThP11 Structural, Optical and Photocatalytic Study of Spray Pyrolysis-Deposited ZnO: Al Thin Films,** ***M. Shahjahan****,* University of Toyama, Japan, *K.R. Khan,* Rajshahi University, Bangladesh, *M.F. Hossain, S. Biswas,* University of Toyama, Japan, *T. Takahashi*, Toyama University, Japan

ZnO is a semiconductor with unique properties such as transparency in the visible and high infrared reflectivity, acoustic characteristics, high electrochemical stability and excellent electronic properties. ZnO has received much attention because of its promising applications of optoelectronic nano-devices, piezoelectric nano-generators, dye-sensitized solar cells, bio-devices and photocatalysts for degradation and complete elimination of environmental pollutants. Porous ZnO films with large surface area have great applications in photovoltaic and photocatalytic devices. Moreover Al-doped ZnO (ZnO:Al) shows lower band gap. In the present study an effort has been made to fabricate ZnO:Al on glass substrate using low-cost spray pyrolysis method with higher surface area. Structural, optical, electrical and surface morphological studies of the fabricated films have been performed. Photocatalytical activity of the fabricated films has been studied. The crystal structure of annealed samples was investigated by X-ray diffraction (XRD). XRD patterns show crystalline nature of the spray deposited ZnO and Al-doped ZnO thin films with three main peaks, (100), (002) and (101) planes. ZnO crystal has wurtzite structure and the calculated lattice constants a and c are 3.242 Å and 5.209 Å respectively and the grain sizes are in the range of 16.75 to 52.19 nm. The surface morphology of the films was observed by a scanning electron microscope. It has been observed that the film surfaces are varied with the deposition conditions and doping concentrations. The spectral absorption coefficient of the ZnO and ZnO:Al films was determined using the spectral data of transmittance and reflectance in the UV-visible wavelength range. The direct and gap energies for ZnO and ZnO:Al were determined and the values obtained are 3.2 eV and 2.88 eV, respectively. Photocatalytic activity of ZnO:Al thin films have been evaluated with various pollutant under UV-visible irradiation.

**SE-ThP12 Strain-Rate Sensitivity of Nanocrystalline Nanolaminates,** ***H.S.T. Ahmed****, A.F. Jankowski*, Texas Tech University

The strain-rate sensitivity of strength is one of the key parameters to understand the deformation mode of nanocrystalline materials. It is widely reported that many nanocrystalline materials strength harden with increasing strain rate. Often, an increasing strain rate exponent is observed as the grain size decreases from the micro- to the nano- scale. This trend suggests that the mode of mechanical deformation is transitioning from within the grains to becoming a grain boundary effect. For nanocrystalline nanolaminates, another dimensional feature becomes significant. The layer pair spacing must now be accounted for in addition to the grain size. This additional nanoscale feature can become especially important when its size decreases below that associated with conventional dislocation-based strengthening mechanisms. We now investigate the hardness of transition metal nanolaminates for which both grain size and laminate dimensions are less than 10 nm. New data is acquired through the technique of nanoscratch testing. We report an increasing rate sensitivity of strength, as measured by the plastic flow associated with hardness, when dimensional features are further reduced to below 10 nm.

**SE-ThP13 Effect of Deposition Temperature on Microvillus-structured InGaN Films Deposited by Glancing-angle Reactive Evaporation,** *H. Takaba,* ***H. Takeuchi****, Y. Inoue, O. Takai*, Nagoya University, Japan

1. Introduction Electrochromic (EC) materials have a unique property of reversible color change with a burst of electrical charge. Much attention has been paid to the EC materials for application to “smart windows”, which control electrically the light and heat through the windows. We have investigated the EC properties of indium nitride (InN). The EC of InN is

based on so-called Burstein-Moss shift induced by alternation of surface adsorbates. We have improved the EC properties of InN both by doping Ga to shift the color-change wavelength region and by introducing a biomimetic structural design in nano order to increase the EC amplitude. In this study, we deposit microvillus-structured InGaN films at some substrate temperatures and investigate the effect of deposition temperature on crystallinity, biomimetic structure and EC properties. 2. Experimental procedure The Ga-doped indium nitride ($In_{1-x}Ga_xN$, $0 \le x \le 1$) films were deposited in a vacuum evaporation system assisted with an active nitrogen source. Indium and gallium were deposited simultaneously from respective crucibles through a downstream of the nitrogen plasma generated from the active nitrogen source at the conditions of the nitrogen pressure of 0.04 Pa and the RF power of 300 W. The substrate holder was rotated at the speed of 10 rpm with the angle against the metal fluxes at 85° in order to synthesize the biomimetic microvillus-like nanostructures, and heated by lamp heater from behind. Crystallinity, microstructure and EC properties of the $In_{1-x}Ga_xN$ films were characterized by XRD, FE-SEM and UV-VIS spectrophotometry, respectively. 3. Result From XRD analysis, we confirmed that the In@1-x@Ga@x@N films prepared at high substrate temperature had higher crystallinity than at non-heated temperature. EC measurements showed that the EC amplitude of InGaN increased with the crystallinity improvement at high Ga composition. However, at low Ga composition, that of prepared at 150°C was larger than at 200°C because the effective surface area decreased due to microstructure evolution.

**SE-ThP14 Surface of Pb1-xSnxTe Films by Pulsed Laser Deposition***,* *M. González-Alcudia,* CICATA-IPN, México*, M. Meléndez-Lira,* CINVESTAV-IPN, México*, O. Calzadilla-Amaya,* Universidad Habana, Cuba*,* ***M. Zapata-Torres***, CICATA-IPN, México

The interest in pulsed deposition was tirggered by the observation that PLD is superior to thermal deposition in inducing layer by layer growth of heteroepitaxial metal films. We present the design of a pulsed laser deposition modified system ( PLD-M ) which is suitable for materials engineering work. Various concepts in growth structure of Pb1-xSnxTe films for PLD-M have been pursued to optimize its performance. A macroscopic description of growth insatabilitiesn of Pb1-xSnxTe films is usually presented in the framework of only 2D nucleation, determined by the supersaturation, limited interlayer mass transport results in nucleation on top of 2D islands before completion of a film layer. Extensive measurements ( AFM, XRD and SEM ) were carried out to test the micro structural characteristics of the Pb1-xSnxTe films. In the case of PLD-M, a typical value for the deposition rate within one pulse is of the order of 10 mm/s and the radius of droplets formed during single pulse irradiation is the r KH ≈ 0.05 μm. These new approaches offer new possibilities for further development of the field in close connection with surface science and materials science.

**SE-ThP15 Enhancement of Hydrophilicity and Photo Catalytic Activities of Nanocrystalline $TiO_2$ Thin Film Doped with Tungsten***, R.R. Pandey, K.K. Saini,* National Physical Laboratory, India*,* ***M. Dhayal***, University of Washington*, C. Chander Kant, S.C. Jain*, National Physical Laboratory, India

In this study tungsten ion doped nanocrystalline TiO2 thin films has been fabricated using dip-coating technique on glass substrates. Surface structure and chemistry of the films was characterized using X-ray diffraction, transmission / scanning electron microscopy, UV-visible spectroscopy, X-ray photoelectron spectroscopy and FTIR. The tungsten ions doping in the film have significant influence on the morphology and surface chemistry. These nanocrystalline films have shown improved activity on the oxidation of organic pollutants possibly due to enhanced surface area with more active site in presence of tungsten.

**SE-ThP16 High Power Pulse Plasma Generator for Material Processing***, R. Chistyakov,* Zond Inc.*,* ***B. Abraham***, Zpulser LLC

High Power pulse Plasma Generator for Material Processing. Roman Chistyakov1,2, Bassam Abraham1,2 Zond, Inc1/Zpulser2, LLC, 137A/137 B High Street, Mansfield, MA 02048, A new high power pulse plasma generator was developed. This plasma generator can generate negative arbitrary voltage pulse shapes in the range 200 – 1500 microsecond in wide range of output power. By applying these pulses to the sputtering magnetron arbitrary pulse power magnetron discharge can be produce. The typical arbitrary voltage pulse shape for magnetron sputtering consists from two stages. The first stage is a low power discharge and the second stage is a high power discharge. The presence of two power stages in one pulse reduces the probability to have arc and increases ionization of sputtered material. High power pulse plasma generator is a switching power supply. User friendly software enables full control of the switching device. This plasma generator was successfully used for different sputtering applications including reactive and non reactive processes. The principals of building arbitrary voltage pulse shapes will be discussed. The examples of different voltage pulse shapes for different sputtering conditions will be presented.

## Surface Science
## Room: Hall D - Session SS-ThP

## Poster Session

**SS-ThP1 Adsorption, Photo-Fragmentation, and Ion-Desorption Pathways of Organic Molecules at Semiconductor Surfaces using Synchrotron Radiation Techniques***,* ***T. Sekiguchi,*** Japan Atomic Energy Agency (JAEA)*, H. Ikeura-Sekiguchi,* National Institute of Advanced Industrial Science and Technology (AIST), Japan*, Y. Baba*, Japan Atomic Energy Agency (JAEA)

The chemistry of organic molecules on semiconductor surfaces has attracted much attention due to the perspective of the molecular wires, self-assembled monomolecular layer (SAM), and semiconductor-organic hybrid formation such as SiC. We have investigated the adsorption interaction, photo-dissociation, and ion-desorption of multifunctional organic molecules such as acetone [(CH3)2C=O] adsorbed on Si substrates. We used synchrotron radiation techniques including polarization-angular dependences of near-edge x-ray absorption fine structure (NEXAFS) and photon-stimulated ion-desorption (PSID). We measured photon-energy dependences of ion yields for a variety of fragments in the carbon 1s excitation region, along with the NEXAFS. We compare results for the following three systems: (1) dissociatively adsorbed monolayered molecules prepared at a room temperature (RT), (2) molecularly adsorbed monolayered molecules prepared by heating condensed molecules very slowly from liquid-N2 low temperatures (LT) to RT, and (3) multilayered molecules prepared at LT. The results showed that mass-patterns and excitation spectra of PSID depend dramatically on the chemical states of adsorbed systems. We conclude that PSID and NEXAFS techniques are useful tools to investigate chemical states such as configuration, orientation, and charge-transfer interaction of adsorbed molecules at surfaces.

**SS-ThP2 AFM Studies of poly-L-lysine Mediated Adsorption of Alginate to Hydrophilic and Hydrophobic Surfaces***,* ***C. Franqui****, H. Applebaum, K.T. Queeney*, Smith College

The poly-L-lysine (PLL)-mediated adsorption of alginate to hydrophobic and hydrophilic substrates is a useful model system for understanding the initial stages of biofilm formation. Work in our lab using a variety of techniques has shown that film continuity and morphology are strongly influenced by the underlying substrate. The current work uses atomic force microscopy (AFM) to examine differences in film morphology as a function both of substrate surface chemistry and of adsorption conditions. On a hydrophobic, electrically neutral alkylsilane monolayer, PLL films adsorbed from pH 11 buffer and air dried exhibit morphologies that are suggestive of polymer shrinking as water is removed from the film, with networks of PLL surrounding regularly-spaced patches of bare surface. The proportion of surface covered by PLL decreases with increasing PLL molecular weight, which suggests stronger PLL-surface interactions for the lower MW polymers. Since adsorption under these conditions is thought to be driven by a transition from alpha helix in solution to random coil for adsorbed PLL, these results may indicated a lesser amount of uncoiling for the larger MW PLL. The role of drying in determining film morphologies is explored by comparing subsequently-adsorbed alginate films on both pre-dried and undried PLL overlayers. On hydrophilic silica PLL adsorbed at neutral pH forms much more uniform films, consistent with strong electrostatic interactions between the positively charged PLL and the negatively charged surface. As ionic strength increases, PLL begins to aggregate on the surface to form a much more discontinuous film, consistent with competition for binding sites between PLL and cations in solution. Alginate adsorption to these PLL overlayers results in more complex morphologies indicative more of isolated molecular adsorption than of true film formation.

**SS-ThP3 Experimental Aspects of Measuring Dissociative Sticking Coefficients of Hydrocarbons on Solid Surfaces with Independently Variable Gas and Surface Temperatures***,* ***V. Johánek****, L. Valadez, G.W. Cushing, I. Harrison*, University of Virginia

The thermal activation of alkanes on transition metals can be studied by a technique of effusive dosing of gases onto the metal surfaces where both gas and surface temperatures are independently variable. Dissociative sticking coefficients, $S(T_g, T_s)$, are measured by monitoring the deposited amount of surface carbon. This relatively simple method allows measurement of dissociative reaction rates of alkanes or other hydrocarbons with about 9 orders of magnitude dynamic range, however, a careful implementation is required to assure good accuracy and relevance. In particular, effects not related to the direct well-defined gas beam or to the surface under study have to be either eliminated or separated which brings several experimental challenges. Ultimately, such $S(T_g, T_s)$ experiments can be used to define reaction rates and transition states for activated dissociative chemisorption reactions that are otherwise difficult to study under ultrahigh vacuum, surface science conditions.

**SS-ThP4 Low Energy Electron Microscopy Study of Adsorbed C on Pt(111)**, ***G.W. Cushing***, *V. Johánek, I. Harrison*, University of Virginia

Methane reforming rates on supported transition metal nanocatalysts at temperatures near 1000 K are apparently limited, in part, by the build-up and dynamics of adsorbed C.[1] We report on the use of a SPECS low energy electron microscope (LEEM) to examine the dynamics and reactivity of adsorbed C on Pt(111) at reforming temperatures. The adsorbed C coverage can be controlled by dosing hydrocarbons and/or oxygen at pressures as high as ~5 x $10^{-8}$ Torr whilst imaging with LEEM.

[1] H. L. Abbott and I. Harrison, "Methane dissociative chemisorption on Ru(0001) and comparison to metal nanocatalysts", J. Catal. 254, 27-38 (2008).

**SS-ThP5 Interaction of Water with BaF$_2$(111) at Ambient Conditions**, ***S. Kaya***, *S. Yamamoto*, Stanford Synchrotron Radiation Laboratory, *J.T. Newberg, H. Bluhm*, Lawrence Berkeley National Laboratory, *A.R. Nilsson*, Stanford Synchrotron Radiation Laboratory

Aggregation of water and ice nucleation on ionic surfaces have been a topic of interest for many years due to their importance in atmospheric and environmental chemistry. However, the fundamental questions such as the structure and chemical composition of thin film water on surfaces in equilibrium with ambient pressure water vapor are still largely unanswered. BaF$_2$(111) is one of the promising model substrates at which two dimensional hexagonal ice growth can be expected due to their matching lattice parameters. By using ambient pressure photoemission spectroscopy (APPES) and O K-edge near-edge x-ray absorption fine structure (NEXAFS) spectroscopy, we have studied the interaction of water with the BaF$_2$(111) surface at water partial pressures up to 1.5 Torr. Water uptake curves indicate that monolayer coverage is achieved at relative humidities lower than 10 %. O K-edge NEXAFS findings reveal that the structure of submonolayer water on the BaF$_2$(111) surface is similar to the topmost surface of hexagonal ice which is lacking two dimensional long range order. Additional water layers obtained at higher relative humidities have slightly different hydrogen bonding structures. In addition, lateral hydrogen bonding network becomes more apparent with increasing water coverage.

**SS-ThP6 LER Reduction by Means of a Grazing Incidence Ion Beam**, ***C. Struck***, *D.N. Ruzic*, University of Illinois, *R.L. Bristol*, Intel Corp.

As lithographic feature sizes continue to increase, the phenomena of line edge roughness (LER) becomes more pronounced. While many efforts are underway to decrease LER from the photoresist, post-develop smoothing techniques may be required to achieve acceptable results. We report on one such technique employing the use of an ion beam at grazing incidence unidirectional with the features. One key potential advantage of this approach over many other smoothing techniques is the ability to smooth LER at relatively long spatial length scales over large sections of, or whole wafers. LER reduction numbers are reported at both short and long spatial wavelengths using Ne, He, and Ar beams. The angle of incidence is varied, as well as ion energy, and process time. LER measurements are taken from top-down analytical SEM measurements and Hitachi image analysis software. Line profile data are taken with the SEM in cross-section mode. Tests have achieved a reduction in LER from 9.8±0.67nm to 5.5±0.86nm for 45nm CDs using an Ar beam at 500eV for 6s at an 85° angle of incidence. A reduction from 10.1±1.07 nm to 6±1.02 nm was shown using an Ar beam at 1000eV for 4s at a 60° angle of incidence.

**SS-ThP7 Modification of PMMA Thin Films with Atomic Oxygen and Ultra-violet Light**, ***H. Yuan***, *D.R. Killelea, S. Tepavcevic, S.J. Sibener*, University of Chicago

The degradation and modification of polymeric surfaces by irradiation, oxygen plasmas and other reactive species have dramatic effect on their physical and chemical behavior. A molecular-level understanding of reactions at the polymer surface is necessary to guide further development of polymers in a wide range of fields, from microelectronics to aerospace. Here, we present the results of a study of photodegradation and oxidation of a model polymeric film. We exposed a poly(methyl methacrylate) (PMMA) film to vacuum ultraviolet (VUV) radiation and a collimated supersonic beam of O($^3$P) oxygen atoms. In separate experiments, we directly measured the mass loss of the film with a quartz-crystal microbalance (QCM) and identify the chemical changes in the PMMA film using in situ infrared spectroscopy. Previous work was limited by the necessity of removing the sample from vacuum for IR analysis; our new in situ IR system lifts this limitation and permits much greater time-resolution in our studies of the polymer modification process. Our analysis has determined the kinetics of the reactions of PMMA with VUV and atomic oxygen, and we have investigated how exposing PMMA films to both atomic oxygen and VUV light alters the polymer properties. We have also found that exposure of the polymer to these two reagents simultaneously results in kinetics that differ from the two individual effects.

**SS-ThP8 State-Resolved Measurements of CH$_4$ Activation on Ni(111) Without Laser Excitation**, ***N. Chen***, Tufts University, *R.R. Smith*, Independent Consultant, *D.R. Killelea*, University of Chicago, *V.L. Campbell, D.F. Del Sesto, A.L. Utz*, Tufts University

We describe experimental work that yields vibrational-state-resolved reaction probabilities for a polyatomic molecule without the need for selective laser excitation of the target state. The method relies on a detailed knowledge of the vibrational structure of the molecule under study, its vibrational cooling dynamics in a supersonic expansion, and an understanding of how individual vibrational states contribute to the state-averaged reactivity measured in the experiment. The reagents in beam-surface scattering measurements of surface reactivity typically have a well-defined translational energy and a narrow distribution of rotational states, but the vibrational state distribution of the reagents remains nearly thermalized at the nozzle source temperature. As nozzle temperatures are raised to access higher incident kinetic energies, the thermal population of excited vibrational states grows. The high vibrational state density of polyatomic molecules can result in hundreds, or even thousands of vibrational states contributing to the measured reactivity. In addition to yielding reaction probabilities averaged over many internal states, the state or group of states that dominate reactivity may vary as a function of incident kinetic energy, even at a fixed nozzle source temperature. Recent results from state-resolved measurements of methane activation on Ni(111) allow us to model vibrational-state-averaged beam-surface data to gain insight into how reactivity scales with increasing vibrational excitation. We use this approach to extract a state-resolved reaction probability for the v=0 vibrational ground state of methane dissociating on a Ni(111) surface. At intermediate nozzle temperatures, only the v=0, $\nu_2$, and $\nu_4$ vibrations have sufficient population to impact reactivity. Non-equilibrium vibrational cooling in the expansion relaxes $\nu_2$ to $\nu_4$. Knowledge of $S_0$ for the v=0 state allows us to extract $S_0$ for the $\nu_4$ vibrational fundamental of the "umbrella" bending vibration.

**SS-ThP9 Interfacial Dynamics of Amorphous and Crystalline Thin Polymer Films**, ***J.S. Becker***, University of Chicago, *M.A. Freedman*, University of Colorado, Boulder, *S.J. Sibener*, University of Chicago

The surfaces of thin polymer films are a complex and dynamic macromolecular interface that have attracted significant attention. Presently, there is poor understanding regarding the modification of dynamics and crystallization at the free polymer surface by dimensional confinement of the polymer into a supported thin film. Helium atom scattering is a uniquely surface sensitive and non-destructive probe of vibrational motion and structure at complex interfaces. Elastic helium scattering reveals surface stiffening of amorphous poly(methyl methacrylate) (PMMA) in molecularly thin films as a function of diminishing film thickness. Furthermore, collisional energy transfer characteristics measured from amorphous PMMA, polystyrene, and polybutadiene films show remarkably similar lineshapes and temperature induced intensity decays, owing largely to the common methylene groups presented at the surface. Additionally, helium scattering provides exquisite sensitivity to surface order and crystallinity. Surface crystallization is presently being measured in thin films comprised of poly(ethylene terephthalate) and compared with related data obtained from glancing-angle Fourier-Transform Infrared Spectroscopy measurements acquired in an ultra high vacuum environment.

**SS-ThP10 Interaction of Water with Pure and Mixed Monolayers of Hydrophobic and Hydrophilic Terminated Alkanethiols on Au(111)**, ***N.M. Barrentine***, *R.L. Grimm, J.C. Hemminger*, University of California, Irvine

The interaction of water adsorbed on self-assembled monolayers (SAMs) with moieties that are either hydrophobic, hydrophilic, or mixtures of both were characterized by temperature programmed desorption (TPD). The SAMs were fabricated on Au(111) from dilute ethanolic solutions of alkanethiols terminated with either a methyl group (hydrophobic) or a polar group (hydrophilic). The goal of our experiments is to understand the interaction of water with localized regions of hydrophilic character on an organic surface as a function of the spatial extent of the hydrophilic region (in the 10's of nanometer size regime). TPD experiments of water desorption from pure hydrophobic surfaces show first order desorption kinetics at low coverage with an activation of energy of ~34 kJ mol$^{-1}$. The peak temperatures seen in the pure hydrophilic TPD spectra are 10-60 K higher than that of the pure hydrophobic case, indicative of a stronger interaction with water. Surfaces functionalized with a mixture of the hydrophobic and hydrophilic terminated alkanethiols display different properties from either of the pure cases and are not well described by simple weighted addition of the two limiting cases. The aim of this work is to develop a well characterized model system that mimics the surfaces of organic-coated aerosols found in the troposphere. These aerosol surfaces are typically hydrophobic when the aerosol is first formed and are thought to become more hydrophilic as the aerosol undergoes varying degrees of oxidation due to reactions with atmospheric oxidizing species such as $O_3$ and OH radicals. We will discuss how our results can be useful in understanding water interactions with atmospheric aerosols.

### SS-ThP11 Optimization of Hardness of Ultra Water Repellent Silica-Based Film by Tuning Surface Structure and Film Matrix, ***H. Sakurai***, *N. Saito, O. Takai*, Nagoya University, Japan

Ultra-water repellent film (UWR) has a water contact angle of more than 150°. The UWR property is governed by the hydrophobic groups and the geometrical structure of the surface. We have successfully fabricated UWR film by microwave plasma enhanced CVD (MPECVD) with trimethylmethoxysilane (TMMOS) as a raw material. However, the UWR film showed a poor mechanical property, because the film was composed of not a continuous film but aggregation of clusters. In order to improve the mechanical property of the UWR film, it is crucial to control the ratio of continuous film and aggregation of clusters in the film. The ratio is strongly related to the surface geometry accentuating the wettability. The large roughness makes the water repellency increase while the hardness of the structure decreases. In this study, we aimed to obtain UWR film with high hardness by tuning the surface structures and film matrix. The UWR film was deposited by MPECVD. A microwave generator (2.45GHz) was used at 250 W. Si wafer was used as substrate. TMMOS was used as a raw material, and Ar was introduced as excitation gas. The partial pressures of TMMOS and Ar were kept constant at 70Pa and 30Pa. And also, the distance between plasma and substrate was constant. The deposition time was changed 3 minutes to 30 minutes to change the surface roughness. Water contact angles on the resulting films were evaluated with a contact angle meter. Hardness of the films was measured by a nanoindentater as Vickers hardness. Surface structures of UWR films were observed by atomic force microscope (AFM). The surface roughness was evaluated by root mean square (RMS). The UWR films with smaller roughness were obtained. Even in the case, the relationship between water repellency and hardness depended on roughness. Smaller roughness would indicate the increase of continuous films. However, the Vickers hardness was not improved drastically. The film matrix was changed by the increase of oxygen and the addition of nitride and so on. The changes of film matrix have a great effect on the improvement of hardness.

### SS-ThP12 Synchrotron Radiation-Induced Reactions of Astrochemical Interest*, ***M.J. Abu Haija***, *R.A. Rosenberg*, Argonne National Laboratory, *P.J. Ryan*, Ames Laboratory

In molecular cloud regions of the interstellar medium (ISM), astronomical observations have revealed a rich chemistry with the detection of over 130 different chemical species ranging from simple diatomic molecules to complex organic molecules such as polycyclic aromatic hydrocarbons (PAHs). These molecules may have been involved in the prebiotic chemistry that led to life's origin. Our approach for simulating such chemistry is to in-situ monitor the x-ray induced chemical reactions of model compounds adsorbed on well-characterized substrates. We are currently pursuing two areas of research in this field. The first one is to understand the source of chirality in prebiotic molecules, which is a subject of great interest to a wide group of researchers. We have recently demonstrated that low-energy spin-polarized secondary electrons, produced by irradiation of a magnetized permalloy substrate can induce chiral selective chemistry of adsorbed (R)- or (S)-2-butanol on permalloy.[1] Using x-ray photoelectron spectroscopy (XPS) to monitor the intensity of the C-O peak, the results showed an enhancement of ~10% in the rate of C-O bond cleavage that depends on the chirality of the molecule and the spin polarization of the substrate secondary electrons. In addition to the C1s XPS measurements used to determine the rate constants, O1s XPS and O1s near edge x-ray absorption fine structure (NEXAFS) as well as x-ray magnetic circular dichrosim (XMCD) measurements were performed. The second area of research is the investigation of x-ray induced chemical reactions of PAHs which are flat molecules based on rings of six carbon atoms. PAHs are of particular interest because they are often used as biomarkers that indicate life. A large variety of these molecules has been detected in meteorites after being delivered to Earth. We will present some preliminary results on the x-ray induced reactions of coronene ($C_{24}H_{12}$). The focus of this work will be to understand the kinetics and mechanisms of this system, as well as other PAHs. Experiments were performed under UHV conditions utilizing both XPS and x-ray excited optical luminescence (XEOL) to monitor the reactions.

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

[1] R.A. Rosenberg, M. Abu Haija and P.J. Ryan, to be published.

### SS-ThP13 CCD for Ion Detection, *O. Hadjar*, ***G. Kibelka***, O.I. Analytical CMS Field Products

Photon imaging based on charged coupled devices (CCD) is a mature technology. Such detectors are used, for instance, in astrophysics instruments as well as in every day consumer products. As a consequence, the CCD underlying functionality is well understood and devices can easily be mass-produced. The common CCD is a fine-pitched, two-dimensional array detector, which can be operated in a vacuum as well as under high pressure. Replacement of the photosensitive layer of the CCD with a metal-oxide semiconductor (MOS) has proven to be a very successful and promising technique for ion imaging. Various instruments based on charge detection can benefit from such a device, particularly mass spectrometers (MS). Fusing the CCD with a miniaturized Matauch-Herzog type MS[1] results in a compact sector-field mass spectrometer with sufficient mass resolution and unmatched duty cycle. Using an electron-impact ion source, formed ions are m/z separated and detected by our CCD located at the focal plane of our instrument. The CCD response can be studied as a function of ion energies and incidence angles. Quantum efficiencies of singly and doubly charged rare gas ions are being investigated and results are compared with electron-impact ionization cross section found in literature.[2] These fundamental studies will increase the accuracy of quantifying abundances of ionic species and can be the base for future improvements.

[1] M. P. Sinha, M. Wadsworth. Rev. Sci. Ins. 76, 025103 (2005).

[2] A. Kobayashi, G. Fujiki, A. Okaji, T. Masuoko. J. Phys. B: At. Mol. Phys. 35 2087 (2002).

### SS-ThP14 Atomistic Approaches to Fischer-Tropsch Model Catalysts, ***B. Wang***, *A. Purdie, M. Caffio, R. Schaub*, University of St Andrews, UK

Fischer-Tropsch synthesis, discovered in the 1920s, is one of the most researched topics within heterogeneous catalysis. Fe and Rh are two widely studied Fischer-Tropsch catalysts. The former strongly dissociates CO and catalyzes the preferential formation of methane and higher hydrocarbons, while the latter exhibits a unique catalytic activity on syngas reactions to form carbon-two oxygenates.[1] It has been demonstrated that additive Fe species to silica-supported Rh catalysts exert a significant promotion in CO hydrogenation by enhancing the yields and unexpectedly increasing the selectivities toward oxygen-containing products such as alcohols[2] In this work, we investigated the FeRh catalyst system within a surface science approach, aiming to get atomic level information on the structure, composition and chemical state of different bimetallic catalysts, and hence an understanding of the Fe promotional role. The nucleation and growth of Fe deposited at room temperature on single-crystalline Rh(111) surfaces (flat and stepped) was investigated as function of Fe coverage. Upon annealing at high temperatures (>600K), STM data confirm the formation of a near surface alloy. By a thorough and systematic comparison of STM images following CO exposure on Rh(111) and on Fe/Rh(111), we investigated the promotional role played by Fe (site specific versus local electronic structure alteration). In an attempt to address more realistic systems, we also performed STM measurements on Rh and Fe physically vapour deposited onto $SiO_2$ thin films. The morphology of the resulting nano-particles, their dispersion and sintering, were studied as function of the Fe:Rh molar ratio. We observed that the addition of Fe dramatically enhances the dispersion of the active Rh loading, concomitant with a significant decrease in average particles size. The implications of our findings are discussed in light of the selective catalysis reported for FeRh systems.

[1] M. Ichikawa, Polyhedron, 7 (1988) 2351.

[2] M. M. Bhasin, et al., Journal of Catalysis, 54 (1978) 120.

### SS-ThP15 Wettability of Self-Assembled Monolayer Surfaces of Alkane Thiols on Au, ***N. Yoshida***, *T. Watanabe*, The University of Tokyo, Japan

Wettability of solid surface has attracted much attention in many fields, from basic surface science to practical uses. Up to now, numerous studies have sought to interpret the static hydrophobicity (contact angle of a droplet and surface energy/surface tention of soild surface) in terms of the interaction between liquid and solid surface. The static hydrophobicity has been well-clarified (controlled by surface energy and morphology), however, the dynamic hydrophobicity (sliding angle and velocity of a droplet), a measure of dynamic adhesive property against water, is still in controversy. Practically, dynamic hydrophobicity does not simply depend on static hydrophobicity. Thus far, no one could completely explain a fact that hydrophobic surfaces of similar water contact angles often show quite different adhesive property against water. In this study, we successfully prepared various hydrophobic surfaces on Au using alkane and fluoroalkane thiols with various adhesive properties against water in terms of solid-liquid interface engineering. We will demonstrate that the dynamic hydrophobicity, a measure of the adhesive property against water, depended on the surface morphology (even of the order of a few nanometers) and surface composition (small amount of polar groups on the surface) and that we could control it independent of static hydrophobicity.

**SS-ThP16 Surface Characterization of Hydrophobic Thin Films Deposited by Various Plasma Polymerization Methods**, ***Y.S. Kim***, *K.-J. Kim*, Korea University, *Y.H. Lee*, Korea Institute of Science and Technology

Plasma polymerization is a thin film deposition process and may be uniformly coated onto any substrate. Plasma polymers generally have different properties from those of conventional polymers due to their unique properties. Plasma polymer films have been used in a variety of applications including barrier coating, protective coating, anti-scratching coating, and dielectric layer in microelectronics. In this study, plasma-polymerized films fabricated by three different type plasma such as inductively coupled plasma (ICP), capacitively coupled plasma (CCP), and pulsed-plasma (PP). Different kinds of hydrocarbon gases and fluorine-containing gases were mixed to investigate their effect on the films. Also, process parameters for plasma polymerization such as gas ratio, gas pressure, plasma power, pulse width, and processing time were investigated. The physical properties of plasma-polymerized thin films made by three different methods were characterized using water contact angle measurement and mechanical test. The adhesion strength between plasma-polymerized thin film and substrate was measured by 90° peel test, and the mechanical properties of plasma-polymerized thin film surface were investigated by indentation. Surface analytical instruments such as Auger electron spectroscopy (AES), x-ray photoelectron spectroscopy (XPS), near-edge x-ray absorption fine structure (NEXAFS), and time-of-flight secondary ion mass spectrometry (TOF-SIMS) were also used to provide useful information about the chemical properties such as surface composition and functional groups.

**SS-ThP18 Fabrication and Characterization of Well-Ordered Model Nanocatalysts using Anodic Aluminum Oxide (AAO) Template**, ***Y.C. Chu***, *C.M. Kim*, Kyungpook National University, South Korea

Heterogeneous catalysts are usually composed of 1 ~ 20 nm metal clusters. It is generally observed that the catalytic activity is greatly affected by the size of metal clusters. It is crucial to control the size of metal clusters in the fundamental studies of catalytic reactions. We fabricated ordered arrays of nonostructures for the study of size-selective model catalysts using porous anodized aluminum oxide (AAO) templates. The AAO templates whose pore sizes were 5 ~ 50 nm were prepared. A silver electrode was sputter-deposited on one side of the templates and Ni, Au and Pt were electrodeposited to produce nanocatalysts with a uniform size. The model catalyst surfaces were characterized by scanning electron microscopy (SEM), transmission electron microscopy (TEM), atomic force microscopy (AFM), X-ray photoelectoron spectroscopy and temperature-programmed desorption (TPD). Catalytic reaction of CO oxidation and propene epoxidation on these model catalyst surfaces will be presented.

**SS-ThP19 Synthesis of Nanostructured CoSb2O6 by a Co-Precipitation Method and its Potential Application as a Gas Sensor Material**, *C.R. Michel, A.H. Martinez-Preciado*, ***H. Guillen-Bonilla***, *J. Rivera-Domíngez*, Universidad de Guadalajara, Mexico

Nanostructured powders of CoSb2O6 possessing the trirutile-type structure, were synthesized by a co-precipitation method, using antimony chloride and cobalt nitrate. During this process a precipitate was obtained when the reagents were mixed in ethanol, which was stirred for 24 h. Microwave radiation at low power was applied for the evaporation which produced a solid precursor. The thermal decomposition of the precursor, from room temperature to 700ºC in air, was made in order to investigate the crystal structure evolution while increasing the calcination temperature. To perform this characterization X-ray powder diffraction was used, resulting that the tetragonal CoSb2O6, with cell parameters a = 4.6544 Å and c = 9.2823 Å, and space group P42/nmn, can be obtain from 600ºC. The observation of the calcined materials by SEM shows that the main microstructure produced corresponds to a filamentary shape, with a length between 100 to 600 nm. The observation by TEM of these filaments revealed that are composed by an arrangement of nanoparticles with an average size of 20 nm. To test CoSb2O6 as a gas sensor material, the powder calcined at 700 ºC was deposited on alumina substrates using the screen-printing method. DC electrical characterization was performed in air, O2 and CO2, from room temperature to 600oC. The dynamic response of resistance was studied by supplying alternatively the gases while recording the electrical resistance; which increased in approximately 1000 ohms when detecting CO2, whereas for O2 the change was in the order of 100 ohms.

**SS-ThP20 Ion Implantation and Microstructure - How Each Affects the Other in Tool Steel**, ***L.A. Autry***, *D.G. Goberman, H.M. Marcus, R.R. Ramprisad*, The University of Connecticut

Ion implantation has been a useful technique for advanced materials processing for many decades. The range of materials that have been ion beam modified covers most classes of materials and many of these classes in great detail. However, with advances in analytical techniques and new manufacturing techniques and objectives, interesting and new observations of ion beam affects are often just waiting to be found. This research has focused on the affect of various ion implanted species on the chemistry and microstructure of tool steel. The inherently heterogeneous microstructure of tool steels affects both the implantation depth and concentration of implanted ions within the steel. This leads to a near surface region where the ultimate affect of ion implantation is, itself, affected by the local microstructure. Small spot surface spectroscopic analysis will be presented which highlights the magnitude of the phenomenon and the implications of this will be discussed. In addition to the affect of heterogeneous microstructures on ion implanted tool steel, the intertwined affect of surface preparation will be discussed. Often surface oxides are removed prior to ion implantation either as a by-product of normal materials preparation or intentionally in order to simplify characterization. However, oxides can be quite adherent and are found on many tool steels in use today. An analysis of ion implanted oxidized steel will be presented and tied into the discussion of how local microstructure can affect ion implantation profiles within tool steel.

**SS-ThP21 Temperature-Dependent Surface Structure and Fermi Level of InGaAs**, *J. Shen*, ***W. Melitz***, *A.C. Kummel*, University of California, San Diego

The Si based MOS field effect transistors (MOSFETs) technology is rapidly approaching its theoretical physical limits. III-V compound semiconductors are known as a potential additional technology platform to silicon. The key to fabricating a practical III-V MOSFET is forming an unpinned oxide-semiconductor interface with low fixed charge. The correlation between the atomic bonding structure and the electronic structure at oxide-semiconductor interfaces is critical to understanding how atomic scale changes in electronic structure can cause localization of electrons or holes at these interfaces. We have used atomically resolved scanning tunneling microscopy (STM) images and scanning tunneling spectra (STS) to determine the atomic and electronic structure of clean InGaAs surface structure and gate-oxide/InGaAs semiconductor interface. Using a low temperature preparation we can get an InGaAs(001)-(2×4) surface reconstruction that is mostly β2(2×4) with some α2(2×4) regions. However these surfaces are very oxygen sensitive and reconstruction is not pure. Then increasing preparation temperature, we can get mixed surface reconstruction structure of InGaAs(001)-(2×4) and (4×2). For even high temperature, we can get pure InGaAs(001)-(4×2) surface reconstruction. Then oxides are deposited on InGaAs surface and STS measurements are being performed to determine the electronic properties of the interface and whether Fermi level is pinning or unpinning.

**SS-ThP22 XPS and Ellipsometry Analysis of Process Variations for Direct Current Plasma Enhanced Chemical Vapor Deposition of Trimethylsilane**, ***P.R. Scott***, *D.M. Wieliczka*, University of Missouri-Kansas City

Thin films were deposited onto Aluminum and Silicon substrates utilizing DC PECVD of Trimethylsilane. The process parameters of gas pressure, discharge voltage, discharge current and deposition time were varied. The films were analyzed using X-ray photoelectron spectroscopy in conjunction with argon ion etching to determine the chemical properties as a function of film thickness and to examine the film-substrate interaction. Spectroscopic ellipsometry was used to obtain the optical properties and film thickness. Results from the comparison and correlation of these film properties to the process parameters will be presented.

**SS-ThP23 Cycloaddition and Cyclocondensation Processes on Silicon: Nitrosobenzene on Si(100)-2x1 and Nitrobenzene on Hydrogen-Terminated Si(100)**, ***K.A. Perrine***, *T.R. Leftwich, C.R. Weiland, R.L. Opila, A.V. Teplyakov*, University of Delaware

Reactions of nitrogen-containing bifunctional molecules with silicon substrates can play an important role in such areas of science and engineering as molecular electronics, surface passivation, and building organic/inorganic interfaces. These nitrogen-containing bifunctional molecules can be attached to the silicon surface via the nitro or nitroso group. The other end of the bifunctional molecule, a phenyl ring, remains intact after the reaction allowing for the model studies of electron transfer processes or for further surface modification. Nitrosoadducts are obtained from two different bifunctional molecules and two different surfaces. Nitrosobenzene reacts initially through a [2+2] cycloaddition on a clean Si(100)-2x1 surface through the N=O group leaving the phenyl ring intact.

The oxygen migrates subsurface leaving the phenylnitrene adduct the dominant product from the reaction leaving the minor presence of the nitrosoadduct on the surface. However, nitrosoadducts are the dominant products from the condensation reaction of nitrobenzene with hydrogen-terminated Si(100). All these products and their distribution on surfaces are verified using X-ray photoelectron spectroscopy (XPS), infrared spectroscopic measurements (FTIR), and density functional theory (DFT) calculations. Analysis of the surface reaction pathways and spectroscopic investigations draw parallels between the nitrobenzene reaction on clean Si(100)-2x1 and hydrogen-terminated Si(100) and nitrosobenzene on clean Si(100)-2x1.

**SS-ThP24 Formation and Collapse of Au/n-Si Schottky-Barrier Contact at the $SiO_2$/Si Interface and Oxidation Kinetics in Au-Contaminated and Thermally Oxidized n-Si (001) Surfaces**, ***S. Shimizu***, *S. Shimada, N. Nagase, M. Muta, I. Ikeda*, Nihon University, Japan

We have investigated an anomalous profile of Au in $SiO_2$/Si region as a function of oxidation temperature and then clarified an oxidation mechanism utilizing ellipsometer, X-ray photoelectron spectroscopy (XPS) and alternating current surface photovoltage (AC SPV) methods. When n-type Si wafers having hydrophobic surface were rinsed in Au aqueous solution (the Au surface concentration = ~2 1015 atoms/cm2) and then thermally oxidized at between 550 and 750C, an Au cluster still resided both at the $SiO_2$/Si interface and the top area of $SiO_2$ film. Most of the Au at $SiO_2$/Si was identified to be detected as the Au cluster which did not make bonds with other elements such as O, H and Si. The Au at the $SiO_2$/Si interface formed Au/n-Si Schottky-barrier, causing depleted and/or inverted layer at the Si surface, thereby, giving rise to an occurrence of a frequency-dependent AC SPV. As the oxidation temperature and time increased, the frequency-dependent AC SPV decreased and disappeared, corresponding to the fact that the Au cluster at $SiO_2$/Si interface decreased and/or disappeared. At oxidation temperatures higher than at 750~800 C, the frequency-dependent AC SPV was not detected. The Au was found to diffuse deeper in both $SiO_2$ bulk and Si substrate as the oxidation advanced. Regarding oxidation kinetics at between 550 and 900C, Au caused a drastic $SiO_2$ growth enhancement for $SiO_2$ thickness less than ~10 nm. This result shows that Au acted as catalyst to promote the initial $SiO_2$ growth at the Si(001) surface. The behavior of the Au in $SiO_2$ layer explained the relationship between oxide thicknesses and oxidation time. Finally, the $SiO_2$ growth mechanism influenced by the addition of Au is proposed.

**SS-ThP25 Oxidation of the PAH Coronene by Ozone and the Hydroxyl Radical**, ***E.R. Mysak***, *J.T. Newberg, J.D. Smith, K.R. Wilson, H. Bluhm*, Lawrence Berkeley National Laboratory

Polycyclic aromatic hydrocarbons (PAHs) are a class of organic pollutants, consisting of two or more fused benzene rings, emitted directly into the atmosphere primarily through incomplete combustion processes and known to have allergenic, mutagenic, and carcinogenic effects. In the atmosphere, smaller PAHs are found primarily in gas-phase, whereas three or four-member ring compounds are partitioned between gas and particulate matter, and compounds with greater than five-member rings mostly reside in the particle phase. The atmospheric fate of these heavier PAHs is governed by heterogeneous reactions between the surface bound PAHs and gas-phase atmospheric oxidants such as ozone, the hydroxyl radical, and nitrates, however, these heterogeneous chemical reactions are relatively poorly understood and studied. In the current study, reactivity of the seven-member ring PAH coronene to oxidation sources ozone and hydroxyl radical is examined. To probe the extent of chemical reaction, product formation, and change in surface morphology as a function of reaction, we examine coronene adsorbed onto various substrates, from both a surface and bulk perspective, with ambient pressure photoemission spectroscopy (APPES) and aerosol mass spectrometry (AMS), respectively. In bulk on-line analysis, a 20nm thick layer of coronene adsorbed onto NaCl seed particles and reacted with either oxidant in a flow tube showed very little reactant conversion to product in the AMS. However, surface analysis by the APPES of the same reaction where coronene was adsorbed onto model substrates showed up to 90% conversion of the carbon species to volatilized or oxidized carbon. Data obtained with these two complimentary bulk and surface techniques provide evidence for a surface selective reaction. Using APPES, we are able observe the two oxidation reactions transforming on different timescales and through differing pathways, resulting in dissimilar final states.

# Thin Film
# Room: Hall D - Session TF-ThP

## Aspects of Thin Films

**TF-ThP1 Surface Roughness of Amorphous Carbon Nitride Films Prepared by rf-Reactive Sputtering**, *S. Kikuchi, M. Aono, N. Kitazawa,* ***Y. Watanabe***, National Defense Academy, Japan

Amorphous carbon nitride (a-CNx) thin films were deposited on silicon single crystal substrates by rf-reactive sputtering method using a graphite target, and after deposition the films were exposed to oxygen plasma so as to be modified on their surface. The effect of the substrate temperatures, deposition time and oxygen plasma treatment on the surface roughness has been studied. The substrate temperature was varied from room temperature to 853 K and the deposition time was changed from 10 to 180 min. Oxygen gas of about 20 Pa was discharged by rf-power and oxygen plasma was generated. Plasma treatment time was changed from 10 to 60 sec. Film composition and the chemical bonding states were analyzed by X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FT-IR). Film surface was observed by atomic force microscopy (AFM). AFM observations has revealed that the as-deposited film surface is uniformly covered with particle-like features in the early stage of deposition and the surface changes to be covered with broccoli-like features with increasing the deposition time and correspondingly the root-mean square roughness (RMS) increases from about 0.5 to 7 nm after 180-min deposition, while the RMS slightly decreases with the substrate temperature under the constant deposition time of 10 min. After exposure to oxygen plasma, the film surface was etched selectively and the RMS increases with the plasma treatment time. It should be mentioned that the etching behavior depends on the film deposition temperatures. XPS studies have shown that the bonding states between carbon and nitrogen change with the deposition temperature. This change may be related to the different etching behavior against oxygen plasma.

**TF-ThP2 Nanotribological Properties and Degradation of Ionic Liquid Films on Magnetic Tapes**, ***M. Palacio***, *B. Bhushan*, The Ohio State University

New magnetic tapes with ultrahigh storage density are expected to encounter increasingly more intolerant head and tape path materials, such that the fatty acid mixtures and fluorocarbons that are currently used as tape lubricants may no longer provide adequate wear protection. Ionic liquids are promising as lubricants for magnetic tapes because of their desirable thermal properties. Characterizing the nanotribological properties and degradation of ionic liquids is a crucial step in evaluating the potential of these novel materials as the next generation lubricant for tapes. In this study, commercial AME tape was lubricated with two ionic liquids, 1-butyl-3-methylimidazolium hexafluorophosphate (BMIM-$PF_6$) and 1-butyl-3-methylimidazolium octyl sulfate (BMIM-$OctSO_4$), and were investigated for the first time with atomic force microscopy. The adhesive and friction properties of the ionic liquids were compared to the perfluoropolyether (PFPE) lubricant Z-TETRAOL. Tape durability studies were conducted by running the lubricated tape samples to failure. The tape life of the lubricated samples was compared to historical data on MP and ME tapes.

**TF-ThP3 Influence of Re-Deposition on Particle Generation**, ***C.F. Lo***, Praxair Electronics

In physical vapor deposition (PVD), depending on the target material, target design and sputtering conditions, the bombarded atoms may re-deposit on to the lower erosion zone of the sputtered target. Due to difference in structure between the sputtering target and re-deposited layer, flaking may occur mainly induced by mismatch of coefficient of thermal expansion, resulting in particles generation and causing defects on substrate. Micro-arcing at the tip of re-deposited nodules is another potential particle source in target sputtering. In this report, re-deposition of many materials used for the semiconductor devices, such as Cu, Ti, Ta, W, WTi, W-Silicide and Cr, were discussed. Direct and indirect evidences of flaking and micro-arcing acting as particle sources to substrate are also presented in this report.

**TF-ThP5 Synthesis of SiGeC Alloy by the Modified Ablation Laser Technique***, ***J.G. Quiñones Galván***, *F. de Moure Flores, E. Mota Pineda, S. Cerón Gutiérrez,* CINVESTAV-IPN, Mexico, *A. Hernández Hernández,* Escuela Superior de Física Matemáticas-IPN, Mexico, *M. González Alcudia,* CICATA-IPN Unidad Altamira, Mexico, *J.J. Araiza Ibarra,* Universidad Autónoma de Zacatecas, Mexico, *M. Meléndez Lira*, CINVESTAV-IPN, Mexico

SiGeC has been the subject of interest because of the possibility of control the stress associated to the deposit of SiGe/Si heterostructures but also for the possibility to modify the SiGe properties to produce light efficiently.

However, the major problem to deposited this alloy in the whole range of compositions is the low solubility of carbon in SiGe. We present the results of the characterization of SiGeC alloys produced by the modified ablation laser technique in which the desired SiGeC alloy composition target is prepared by ball milling[1]. The target is prepared as a powder of the right composition and subject to the ablation process. Films of the $Si_{1-x-y}Ge_xC_y$ alloys were prepared with $0.1<x<0.3$ and $0<y<0.1$. Samples were characterized by X ray diffraction, atomic force microscopy, IR, Raman and photoluminescence spectroscopies. The results are discussed in function of the amount of substitutional carbon.

[*] This work is partially funded by CONACyT- Mexico.

[1] M. González-Alcudia, A. Márquez-Herrera, M. Zapata-Torres, M. Meléndez-Lira and O. Calzadilla-Amaya, Adv. in Tech. of Mat. And Mat. Proc. J. 9, 81 (2007).

### TF-ThP6 Surface, Interface, and Bulk Characterization of ALD Cu Films and PVD Dielectric Films, ***L. Zhang***, *K. Lloyd, G. Blackman, L. Bao, J. Thompson, M. Plummer, D. Brill, J. Ryley, D. Reardon*, DuPont

Surface and interface properties of thin films play an important role in a variety of existing and emerging industrial applications, including the development of semiconductor devices, surface coatings, heterogeneous catalysts, polymers, biological materials, and medical devices. Among these applications, the surfaces and interfaces of these materials often control device or part performance, therefore quantitative chemical and structural characterization in the near surface region are critical to quality. This presentation will cover two topics. The first part will focus on the applications of applying integrated methods/techniques to characterize surface roughness, film quality and thickness of ultrathin copper films prepared by the Atomic Layer Deposition (ALD) process. The second part of the presentation will discuss the surface and interface characterization of dielectric films prepared by the Physical Vapor Deposition (PVD) method.

### TF-ThP7 Characteristics of the Top-Emitting Organic Light-Emitting Diodes Based-on the Electronic Structure of the BaO-on-Alq3 Interface, ***J.T. Lim***, *G.Y. Yeom*, Sungkyunkwan University, Korea

Top-emitting (TE) type of organic light-emitting diode (OLED) have been actively developed in recent years, to improve aperture ratio to the top cathode direction in active matrix (AM) displays. Therefore, developing thin semitransparent conducting cathodes (STCCs) have become one of the essential key-element technologies to obtain a high light out-coupling of the devices. In this study, STCC of the BaO/Ag (20 nm)/ITO (100 nm) structure were used to fabricate the TEOLED. The TEOLED structure is consisted of glass/Ag (150 nm)/tin-doped indium oxide (125 nm)/4,4',4''-tris[2-naphthylphenyl-1-phenylamino]triphenylamine (2-TNATA, 30 nm)/4,4'-bis[N-(1-napthyl)-N-phenyl- amino]-biphenyl (NPB, 18 nm)/tris(8-quinolinolato)aluminum (III) (Alq3, 62 nm)/BaO (x nm)/Ag (20 nm)(x: 0, 0.5, 1, and 1.5 nm)/ITO (100 nm). The device with 0.5-nm-thick BaO showed the highest driving performance as the luminous efficiency of 2.7 % and the maximum luminance of 47000 cd/m2, compared with other devices. The driving performance of these devices can be explained by analyzing as electronic structures of the BaO-on-Alq3 interface. In the ultraviolet photoemission spectroscopy (UPS) study, the barrier height of an electron injection (ΦnB) from the BaO/Alq3 interface to the Alq3 layer is increased with increasing the coverage of BaO on Alq3. In the X-ray photoemission spectroscopy (XPS) studies of the O, N, and Ba core levels, the staged interface reaction of two steps was observed, which shows the formation of stable radical anion at low BaO coverage of below 0.5 nm.

$Alq_3$. $cd/m^2$. $\varphi_n{}^B$.

### TF-ThP8 Influences of Ceria-Mixed Abrasive Slurry on the Oxide-Chemical Mechanical Polishing, ***S.J. Han***, *Y.K. Lee, S.W. Park,* Chosun University, Republic of Korea, *Y.J. Seo,* Daebul University, Republic of Korea, *W.S. Lee*, Chosun University, Republic of Korea

In this paper, we have studied the chemical mechanical polishing (CMP) characteristics of mixed abrasive slurry (MAS) retreated by adding of ceria (CeO2) abrasives within 1:10 diluted silica slurry. The slurry designed for optimal performance should produce reasonable removal rates, acceptable polishing selectivity with respect to the underlying layer, low surface defects after polishing, and good slurry stability. The modified abrasives in MAS are evaluated with respect to their particle size distribution, surface morphology, and CMP performances such as removal rate and non-uniformity. As an experimental result, we obtained the comparable slurry characteristics compared with original silica slurry in the viewpoint of high removal rate and low non-uniformity.

### TF-ThP9 Improvement of Tetra-Ethyl Ortho-Silicate Oxide - Chemical Mechanical Polishing Characteristics According to the Cerium Oxide Dispersion Time, ***Y.K. Lee,*** *S.J. Han, S.W. Park,* Chosun University, Republic of Korea, *Y.J. Seo,* Daebul University, Republic of Korea, *W.S. Lee*, Chosun University, Republic of Korea

CMP (chemical mechanical polishing) process has been attracted as an essential technology of multi-level interconnection. However, the COO (cost of ownership) is very high, because of high consumable cost. Especially, among the consumables, slurry dominates more than 40 %. So, we focused how to reduce the consumption of raw slurry. In this paper, CeO2 abrasive was added de-ionized water (DIW) and pH control as a function of KOH contents. And then, we have discussed the CMP characteristics as a function of abrasive dispersion time. We have also investigated the possibility of CeO2 - mixed abrasive slurry for the oxide CMP application. Note: Requested a Poster Session.

### TF-ThP10 Influence of Ar/$O_2$ Gas Ratio on the Performance of Sputtered-Deposited $TiO_2$ Electrodes for the Application of Dye-Sensitized Solar Cells, *M.F. Hossain*, ***S. Biswas***, *M. Shahjahan, T. Takahashi*, University of Toyama, Japan

Dye-sensitized solar cells (DSCs) have attracted great interest because of their potential application as a cost effective and alternative to the p-n junction solar cells. Conventional technology of DSCs employs colloidal films of titanium oxide ($TiO_2$) to which a ruthenium dye is attached. In such conventional processes, porous $TiO_2$ electrode also gives rise to several undesired characteristics, such as low conductivity and charge density and non-uniform over the large area. Reactive magnetron sputtering is a very promising technique for large-area uniform coating to preparation high quality $TiO_2$ thin films with strong adhesion to substrate and it has potential to control the crystallographic phase and micro-structure through the process of modification of different sputtering parameters. In this study, an effort has been made to fabricate the DSCs with sputter-deposited $TiO_2$ electrode. Nanoporous $TiO_2$ electrodes were successfully deposited on $SnO_2$:F coated glass substrate by facing target reactive sputtering technique with 500 W dc input power, 2.0 Pa sputtering pressure and various sputtering Ar/$O_2$ gas ratios such as, 8:2, 7:3 and 6:4. Ruthenium complex based-dye was used to sensitize these electrodes and carbon paste on $SnO_2$:F coated glass was used as a counter electrode. The amount of dye incorporation was found to be highly dependent on the microstructure of the film with various gas ratios, as apparent from optical measurements. The surface morphology of the films has been observed by atomic force microscope and field emission scanning electron microscope. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different $TiO_2$ thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells with $TiO_2$ electrodes deposited at various gas ratios is discussed with the analysis of different microstructure of the $TiO_2$ electrodes and the corresponding dye-incorporation.

### TF-ThP12 The Influence of N-dopping for Titanium Dioxide Thin Films on Photo-functional Properties, ***K. Tanaka***, *I. Takano*, Kogakuin University, Japan

$TiO_2$ is anticipated as one of materials which are alternative for existing solar cell technology based on silicon. $TiO_2$ shows relatively high reactivity and chemical stability under UV light whose energy exceeds the band gap of 3.2 eV in the anatase crystalline phase. The sun can provide an abundant source of photons. however, UV light accounts for the only small fraction (～5 %) of the sun's energy compared to the visible region (45 %). Many techniques have been examined to achieve this purpose, including the doping of $TiO_2$ with transition metals (such as Cr, Fe, Ni, V), but these doped materials suffer from thermal instability and an increased number of carrier recombination centers. Many research groups proposed to replace Oxygen by another anionic species (such as C, P, S, N, F) rather than incorporating transition metals into $TiO_2$. Especially, Nitrogen-doped $TiO_2$ is often used to improve the photocatalytic properties of $TiO_2$ in order to achieve visible light response.[1] In this study, the Nitrogen-doped $TiO_2$ film has been prepared by reactive magnetron sputtering using a Ti target in an Ar/$N_2$+$O_2$ gas mixture. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and X-ray diffraction, respectively. Chromatic change of a methylene blue solution was applied to a photocatalytic property. Light irradiation to the $TiO_2$ film in a methylene blue solution was carried out using a commercial sterilizing lamp as ultraviolet light and a commercial fluorescent lamp as visible light. Transmittance of a methylene blue solution was measured by a spectro photometer. Furthermore, photocurrent between the $TiO_2$ film and a platinum electrode was measured by a volt-ampere characteristic using an unresisted ammeter in a KCl solution of 0.5 mol/ℓ. In the case of the Nitrogen-doped $TiO_2$ film, the higher photocatalytic property and photocurrent under a sterilization lamp were obtained at $N_2$ gas flow rate of 0.6 sccm and 0.4-0.5 sccm, respectively. In the case of a fluorescent lamp, the photocatalytic property showed lower transmittance and photocurrent as compared with that of a sterilization lamp. But transmittance and photo current showed the maximum value at $N_2$ gas flow rate around 0.5 sccm, so Nitrogen-dope effect was confirmed under a fluorescent lamp.

[1] R.Asahi, et al.; Science, 293(2001)269.

**TF-ThP13 The Structural, Electrical and Optical Properties of ATO Films Prepared at Room Temperature by Radio Frequency Magnetron Sputtering for Transparent Electrodes,** ***S.U. Lee***, Sungkyunkwan University, Korea, *W.S. Choi,* Hanbat National University, Korea, *H.J. Kim, B. Hong*, Sungkyunkwan University, Korea

Antimony-doped tin oxide (ATO) films were prepared on a 7059 Corning glass substrate by the radio frequency (RF) magnetron sputtering method using a SnO2 target mixed with Sb of 6 wt% at room temperature. The working pressure was varied from 5 to 15 mTorr in steps of 5 mTorr, and the RF power was varied from 100 to 175 W in step of 25 W at room temperature. The thickness of the deposited ATO films was about 150 nm ± 10. X-ray diffraction (XRD) measurements showed ATO films to be crystallized with a strong (101) preferred orientation as the RF power increased. The spectra revealed that the deposited films were polycrystalline and they retained the tetragonal structure. The grain size, which was 23.2 nm, was calculated from the XRD spectra using the Scherrer equation. ATO film deposited at a working pressure of 5 mTorr and RF power of 175 W showed the lowest resistivity of 8.6 x 10^-3 ohm.cm and the optical transmittance was 86.5 % in the visible range.

**TF-ThP14 Interface Control Effect of Nitrogen-doped Diamond-like Carbon by Ion Beam Assisted Deposition Method,** ***K. Harada***, *I. Takano*, Kogakuin University, Japan

DLC (Diamond-like Carbon) constituting a class of new materials is an amorphous carbon including hydrogen and has similar properties of matter with a diamond. DLC film was formed by the ion beam evaporation method in the early 1970's,[1] and after that has been manufactured by various methods such as CVD (Chemical Vapor Deposition) or PVD (Physical Vapor Deposition). Because the representative mechanical property of DLC is to show the high hardness and low friction coefficient, DLC is applied in various filed such as motor parts or tools. Also the electric properties of DLC are anticipated as a field emission source. In this study, mechanical properties were investigated about the interface between the DLC film and the substrate controlled by the ion beam assist. The ion beam assisted deposition method has many parameters on the film formation condition in comparison with other dry process methods. Therefore this method was anticipated in production of new characteristics such as a high adhesion film. The interface control was performed by changing two procedure. The first process was performed by an accelerating voltage of 12 kV with a current density of 40 μA/cm$^2$ to obtain the high hardness property. The second process was performed by an accelerating voltage of 5 kV with a current density 40 μm/cm$^2$ to obtain the low friction property. An $N_2^+$ ion beam and a $C_7H_8$ gas atmosphere were used on this ion beam assisted deposition method. Composition and microstructure of these films were investigated by X-ray photoelectron spectroscopy and Raman spectroscopy. The hardness was measured from an indentation method with a Knoop indenter. The friction coefficient was measured for an SUJ2 ball with a constant load 0.98 N until the sliding distance reached a length of 10m. As for the sample formed the mixing layer at the first process, mechanical properties were improved in the hardness and the friction coefficient. The Knoop hardness of the film showed 23 GPa. The sample formed using both of first process and second process showed 0.194 in the friction coefficient, because mechanical properties were improved by the interface condition. The depth profile of the mixing layer showed gradual change of C and Fe (as substrate material) in comparison with a sumple without mixing layer.

[1] S. Aisenberg , R. Chabot : J. Appl. Phys., 42, 2953 (1971).

**TF-ThP15 In Situ Spectroscopic Ellipsometry Studies of the Oxidation of Nickel Thin Films,** ***J. Rhim***, *S. Lee, H. Jeong,* Hanyang University, South Korea, *D. Kim,* Ewha Womans University, South Korea, *I. An*, Hanyang University, South Korea

Nickel oxide film is an attractive material for electrochromic devices as well as resistance random access memory devices. In this work, e-beam evaporated nickel films are thermally oxidized in oxygen ambient at various temperatures. In situ spectroscopic ellipsometry is employed to study the oxidation process of nickel films. The optical and microstructural properties of nickel oxide films are deduced and these are compared with the electrical properties. When the nickel film is not fully oxidized, the optical properties of nickel oxide show the inclusion of nickel element. This film shows low resistivity and poor switching characteristics.

**TF-ThP16 Study of Vanadium Oxide Thin Films Deposited by Pulsed DC Sputtering using a $V_2O_3$ Target,** ***K.E. Wells***, *S.S.N. Bharadwaja, M.W. Horn*, The Pennsylvania State University

Uncooled infrared focal plane arrays (IRFPAs) are the critical technology for night vision cameras needed for military and civilian applications. The two most widely used temperature sensitive imaging materials are vanadium oxide and amorphous silicon typically deposited by reactive ion beam sputtering and PECVD respectively. For future applications requiring higher speed and/or sensitivity, materials with high temperature coefficient of resistance (TCR) may be desirable. In this work, vanadium oxide thin films were made at room temperature by reactive pulsed DC (225 kHz) magnetron sputtering of a $V_2O_3$ target with 200 W power. Total pressure and partial pressure of oxygen were varied during deposition to determine their effects on the films properties. The TCR and resistivity values of the films were in the range of -3 to -5% ($K^{-1}$) and 10- 200 kΩ-cm respectively. Both Atomic Force Microscopy (AFM) and Field Emission Scanning Electron Microscopy (FESEM) data established that the microstructures of the films follow the structure zone model with increased columnar size as total pressure is increased. Spectroscopic ellipsometry analysis indicated significant variation in the dielectric functions in the $VO_x$ films with similar electrical properties. We attribute this variation to either differences in porosity or oxygen content. The crystallinity of the films, evaluated by High Resolution Transmission Electron Microscopy (HRTEM) studies, was found to be substrate dependent. Films deposited for various durations with the same deposition parameters showed a lower resistivity with increased thickness.

**TF-ThP17 Atomic Layer Deposition of Lanthanum Based Oxides for High-K Gate Dielectrics,** ***A. Hande***, *B. Lee, H.C. Kim, R.M. Wallace, J. Kim,* The University of Texas at Dallas, *X. Liu, M. Rousseau, J. Yi, D.V. Shenai, J. Suydam*, Rohm and Haas Electronic Materials, LLC.

Lanthanum oxide ($La_2O_3$) is gaining importance as one of the promising high-k candidates due to its superior properties such as a high dielectric constant (~27), large band gap and high electrical breakdown field strength. However, the hygroscopic properties of $La_2O_3$ leads to the formation of lanthanum hydroxide ($La(OH)_3$) which causes deterioration of electrical properties such as, permittivity. Additionally, several studies have reported that a La based CVD process result in a high C concentration in the deposited films. In order to overcome these issues, we investigate two different processes; one is alternating layers of $La_2O_3$ and $Al_2O_3$ to form nano-laminate ($La_xAl_yO_3$) structures and the other is employing ozone as the oxidant. In this study, we deposited $La_xAl_yO_3$ films using atomic layer deposition (ALD) on H-terminated p-type Si (100) substrate using tris(N,N'-diisopropylformamidinato) lanthanum, $La(iPrfAMD)_3$ as the La precursor while water and ozone employing as the oxidant. The physical properties of the deposited La-oxide using various characterization techniques such as HR-TEM, XPS, and XRD as well as electrical characteristics will be presented. Particularly, our in-situ XPS half-cycle study provides an insight on chemical composition modulation based on different process sequence. Acknowledgement: Rohm and Haas Electronic Materials, LLC. for financial support and Toshiba Mitsbushi Electric Industrial Systems Corporation (TEMIC) for providing a ozone generator (OP-H250 LT) for a high concentration ozone.

**TF-ThP18 Integrated UHV/ALD Reactor for Growth of Oxide Materials,** ***K. Pradhan***, *A.E. Wierzbinski, P.F. Lyman*, University of Wisconsin-Milwaukee

We have constructed a novel chemical reactor for controlled growth of crystalline oxide layered structures using Atomic Layer Deposition. The instrument operates in the viscous flow regime, and the design is based heavily upon that of Elam, Groner, and George.[1] However, we have interfaced this reactor to an existing UHV analytical chamber. The combination allows us to investigate not only the as-grown films, but also to study, on an atomic scale, the intermediate reaction sequences. Moreover, we can use established UHV techniques to prepare a well-defined starting surface for subsequent growth, and are able to modify the substrate at arbitrary points in the growth sequence. Initial results on the growth of ZnO films will be reported.

[1] J.W. Elam, M.D. Groner, and S.M. George, Rev. Sci. Instrum. 73, 2981-2987 (2002).

**TF-ThP20 Deposition and Etching of Hexagonal and Cubic Boron Nitride,** ***M. Darnon***, *D.A. Neumayer, G. Gibson, Y. Zhang*, IBM Research

Boron nitride is a material presenting a high thermal conductivity, a low dielectric constant and a high young modulus. Those properties make it a good material to be used in integrated circuits technologies. We present here a process to deposit cubic or hexagonal boron nitride from a high density plasma. The deposition is performed using an ultima high density plasma chamber from Applied Materials. We also present the etching properties of both phases of Boron Nitride using halogenated plasmas. The etching is performed in a DPS chamber from Applied Materials, using a 20 mTorr plasma, with 500W of source power and 100W of bias power. During the deposition, phase formation is found to be critically dependant on diborane, nitrogen and argon gas ratios and the bias utilized during deposition. Cubic boron nitride formation is found to be favored at the deposition/sputtering regime. A density of 2.9 g/cm$^3$ for cubic boron nitride and of 1.8 g/cm$^3$for hexagonal boron nitride is measured by XRR. The etch rate of hexagonal boron nitride is measured by ellipsometry. HBr/Ar plasmas present a very low etch rate (21nm/min). Addition of 25 sccm of $Cl_2$ into the plasma doubles the etch rate. Fluorine-based plasmas etch much faster boron nitride than Bromine- or Chlorine-based plasmas. An eth rate of 146 nm/min is obtained using $CF_4$/Ar, and the etch rate increases up to 511 nm/min with $SF_6$/Ar plasma. The substitution of $CF_4$ by a polymerizing gas such as $CH_2F_2$ leads to a decrease of boron nitride etch rate. The etch rate of cubic boron nitride is also measured. A ratio of 1.2 between hexagonal and cubic boron nitride etch rates is always obtained. Since the density ratio is 1.6, we can say that the structure of cubic boron nitride enhances its etch yield compared to hexagonal boron nitride. Thanks to the deposition and etching processes presented here, the integration of boron nitride in microelectronics technologies can be considered.

**TF-ThP21 Enhancement of Crystal Growth in μc-Si:H Thin Film Deposition by H Radical-Assisted Magnetron Sputtering and the Plasma Diagnostics**, *K. Fukaya,* ***K. Sasaki,*** *A. Tabata,* Nagoya University, Japan, *N. Knake*, Ruhr-Universität Bochum, Germany

Silicon thin films are promising materials for TFTs and solar cells. It is desirable to deposit Si thin films with good electrical characteristics onto various substrates such as a glass at a low temperature. Magnetron sputtering deposition is useful to prepare silicon thin films because of the advantage in not using explosive gases and consequently, a low equipment cost. We measured the Si atom density in rf magnetron sputtering plasmas with a Si target and Ar/$H_2$ mixture gas by laser-induced fluorescence (LIF) spectroscopy. As a result, we found that the sputtering yield in the Ar/$H_2$ mixture discharge was higher than that in the pure Ar discharge. This suggests that sputtering in the Ar/$H_2$ mixture discharge is not simple physical sputtering but a process similar to reactive ion etching (RIE). Since the products of RIE are not Si atoms but molecular species $SiH_x$ (typically $SiH_4$), the deposition mechanism similar to PECVD would be expected in magnetron sputtering of a Si target with the assist of chemical reactivity of H atoms. The objective of this work is to develop a new Si sputtering deposition system employing an H radical source. We expect the enhancement of the RIE effect by injecting additional H radicals produced in an ICP radical source. We prepared Si thin films by using simple sputtering with Ar/$H_2$ mixture gas and H radical-assisted sputtering. In the case of the simple sputtering, an amorphous film was deposited at a low gas pressure of 5 mTorr. The crystalline volume fraction ($X_c$) increased with the gas pressure from 10 to 200 mTorr, and was saturated at gas pressures above 200 mTorr. In the case of the H radical-assisted sputtering, the $X_c$ increased steeply with the gas pressure from 3 to 5 mTorr, and was saturated at gas pressures from 5 to 500 mTorr. It should be noted that the films deposited by the H radical-assisted sputtering crystallized even at gas pressures below 3 mTorr, where the film deposited by the simple sputtering did not crystallize. This result may be attributed to both or one of the following two effects. One is the supply of H radicals produced in the radical source to the growing film surface. The other effect is the enhancement of the production of molecule species $SiH_x$ by the RIE effect. The increases in the densities of molecular species $SiH_x$ may result in the enhancement of the H coverage on the growing film surface.

**TF-ThP22 Fabrication and Characterization of ZnO:(Ag-nano-particles) Thin Films Deposited by Spray Pyrolysis**, *G. Alarcon, J. Guzman-Mendoza, M. Aguilar-Frutis, E. San Martín-Martínez, L. Ortega,* CICATA, IPN, Mexico, ***C. Falcony***, CINVESTAV-IPN, Mexico

Zinc oxide thin films with and without the addition of silver (Ag-nano-particles or AgNO3) were deposited using the ultrasonic spray pyrolysis technique using Zn(acac), in the temperature range from 400 to 550 ºC. The optical, structural and electrical properties of the films deposited were studied. The addition of silver was performed through either a solution containing a dispersion of Ag nano-particles or an AgNO3 solution, sprayed in parallel to the Zn containing aerosol. A comparison between both types of films, as well as with those without silver will be presented. The films resulted dense and transparent in all the cases. The as deposited photoluminescence characterization of the films was measured at room temperature presenting the characteristic peaks 514 and 390 nm associated with ZnO. The electrical characterization of the films was carried out by means of Impedance Spectroscopy. In addition, a structural characterization consisting of X-ray diffraction, energy dispersive spectroscopy, and scanning electron microscopy was also performed in the films.

**TF-ThP23 Growth Rate Induced Epitaxial Orientation of Cerium Oxide Thin Films on Sapphire (0001)**, ***P. Nachimuthu,*** *S.V.N.T. Kuchibhatla, F. Gao, V. Shutthanandan, M.H. Engelhard,* Pacific Northwest National Laboratory, *Z.Q. Yu,* Nanjing Normal University, China, *C.M. Wang*, Pacific Northwest National Laboratory, *S. Seal,* University of Central Florida, *S. Thevuthasan, W. Jiang*, Pacific Northwest National Laboratory

Cerium oxide based materials are widely used in catalysis, solid oxide fuel cells (SOFCs), and for microelectronic applications. Performance of this functional oxide in various applications is dependent on the crystallographic planes of ceria and their participation in various chemical reactions. High-quality ceria ($CeO_2$) films were grown on sapphire, ($Al_2O_3$), (0001) substrates using oxygen plasma-assisted molecular beam epitaxy. The epitaxial orientation of the ceria films has been found to be (100) and (111) at low (< 8 Å/min) and higher growth rates (up to ~30 Å/min), respectively. Reflection high energy electron diffraction (RHEED) measurements show that $CeO_2$ (100) film grows as three-dimensional islands, while $CeO_2$ (111) proceeds with layered growth. In $CeO_2$(100) films, although the growth appears to be 3-D island growth, Rutherford backscattering spectrometry (RBS) measurements along channeling geometry clearly demonstrates that the films have high crystalline quality in comparison to $CeO_2$(111) films. X-ray diffraction (XRD) measurements show that there are three in-plane domains in the $CeO_2$ (100) film and those are attributed to the three-fold symmetry in $Al_2O_3$ (0001) surface. Molecular dynamics (MD) simulations have been carried out to understand the stability of different orientations of ceria on the sapphire (0001) substrate. The experimental observations have been supported very well by the simulations. Excellent oxygen sub-lattice match between sapphire and ceria are proposed as a major driving force for achieving high quality epitaxial films, as opposed to oriented, polycrystalline films. High resolution transmission electron microscopy (HRTEM), atomic force microscopy (AFM) measurements have been carried to study the structure and surface morphology of the ceria films. X-ray photoelectron spectroscopy measurements were used to find the oxidation state of cerium in the as-grown films.

**TF-ThP24 Preparation of Very Thin GZO Transparent Electrodes with a Low Resistivity by a VAPE Method**, ***T. Minami***, *T. Miyata, T. Ito, Y. Honma*, Kanazawa Institute of Technology, Japan

Although transparent conducting impurity-doped ZnO thin films with a low resistivity have been prepared even on low temperature substrates, there is still a problem of the resistivity of the deposited films considerably increasing as the thickness is decreased, irrespective of the deposition methods used. This paper describes the improvements in the thickness dependence of resistivity as well as in other properties obtained in very thin low resistivity Ga-doped ZnO (GZO) thin films prepared using a newly developed vacuum arc plasma evaporation (VAPE) method. It should be noted that in film preparation by VAPE, the substrate normally must rotate or travel linearly during the deposition in order to improve distributions in film thickness and electrical properties across the substrate surface. In this work, however, the substrate remained fixed at a specific position during each deposition. The relative position between the flow direction of the arc plasma and the substrate surface and the VAPE method deposition conditions were optimized to further improve the thickness dependence of the resistivity in transparent conducting GZO thin films deposited on glass substrates. It was found that the obtained resistivity of GZO films deposited with a thickness below about 50 nm at a pressure of 0.15 Pa was strongly dependent on the substrate position relative to the arc plasma flow; it also was affected by the substrate temperature and the Ga content doped into deposited films. In addition, the obtainable resistivity is related to the crystallographical structure, crystallinity and surface morphology of deposited GZO thin films. A resistivity as low as $5X10^{-4}\Omega$cm was obtained in GZO thin films prepared with a thickness of approximately 30 nm under the optimized substrate position and deposition conditions.

**TF-ThP25 Relationship Between Oxide Targets and Properties of Impurity-doped ZnO Thin Films Deposited by DC Magnetron Sputtering**, ***J. Oda***, *T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

This paper describes the relationship between the targets used and the obtained properties of transparent conducting impurity-doped ZnO thin films prepared by a dc magnetron sputtering (dc-MS) deposition method using various sintered oxide targets. The oxide thin films were deposited on glass substrates using a dc-MS apparatus with various sintered impurity-doped ZnO targets; both the target and substrate were fixed during the depositions. In this work, we used various commercially available high-density sintered impurity-doped ZnO disk targets (diameter of about 150 mm). All thin films were prepared with a thickness in the range from 30 to 200 nm; the substrate temperature was controlled to a constant 200ºC during sputtering depositions. It was found that the amount of observable arcing generated during the sputter deposition was considerably dependent on the targets used; in addition, it always increased as the supplied dc power was increased. The obtained minimum resistivity (the resistivity near the substrate location that corresponds to the target center) and the spatial distribution of resistivity on the substrate surface in deposited impurity-doped ZnO thin films were both dependent on the targets used; the varied target properties included density, resistivity and the kind and content of doped impurity. In addition, the film thickness dependence of the obtained resistivity and the stability of the resistivity during long term tests at high temperature in a highly moist environment were considerably affected by the targets used. Improvements in the thickness dependence and the distribution on the substrate surface of resistivity were successfully obtained by varying the target properties. The obtained improvements in deposited films will be discussed on the basis of the relationship between the properties found in both the deposited films and the targets used.

**TF-ThP26 Transparent Conducting Si-co-doped AZO Thin Films Prepared by Magnetron Sputtering Using AZO Powder Targets Containing SiC**, ***J. Nomoto***, *T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

Transparent conducting impurity-doped ZnO thin films are the best, and only practical, indium-free candidate suitable as a substitute for indium-tin-oxide (ITO) thin films used as transparent electrodes in liquid crystal displays (LCDs). However, they have not yet been used practically in LCD applications because of important obstacles such as a spatial distribution of resistivity and insufficient stability of resistivity in impurity-doped ZnO thin films prepared on low temperature substrates by conventional magnetron sputtering depositions. For the purpose of resolving these problems, we have demonstrated a new sputtering deposition technique that was developed to improve both the spatial distribution and the stability in resistivity; transparent conducting Al- and Si-co-doped ZnO (AZO:Si) thin films were prepared on glass substrates at approximately 200°C by rf magnetron sputtering using a powder mixture of ZnO, $Al_2O_3$ and carborundum (SiC) as the target. The SiC content was varied, but the $Al_2O_3$ content was held constant. It was confirmed that the Al and Si contents (Al/(Al+Zn) and Si/(Si+Zn) atomic ratios) in the deposited thin films are approximately equal to those of the powder targets used, but carbon was not detected in all the deposited films. It was found that the spatial distribution of resistivity improved as the Si content of deposited films was increased up to approximately 0.75 at.%; the resistivity of deposited films decreased at the location on the substrate surface corresponding to near the erosion area on the target. This decrease in resistivity is attributed to increases of both carrier concentration and Hall mobility. Thus, the improvement of resistivity distribution obtained in the newly developed sputtering deposition technique may be due to a reducing effect originating from the carbon produced by sputtering the SiC containing AZO target during the film deposition. In addition, it was found that the stability of resistivity during long term tests at a high temperature in a highly moist environment of Si-co-doped AZO thin films is better than that of non-Si-co-doped AZO films prepared with the same thickness under the same deposition conditions.

**TF-ThP27 Transparent Conducting AZO Thin Films Prepared Using Oxide Targets Sintered by Millimeter-wave Heating**, ***T. Miyata***, *Y. Hara, K. Okada*, Kanazawa Institute of Technology, Japan, *H. Abe*, Fuji Dempa Kogyo Co. Ltd., Japan, *T. Minami*, Kanazawa Institute of Technology, Japan

In this paper, we describe the preparation of transparent conducting Al-doped ZnO (AZO) thin films by magnetron sputtering deposition (MSD) and pulsed laser deposition (PLD) using AZO targets sintered with a newly developed millimeter-wave (28GHz) heating technique. For the purpose of evaluating the millimeter-wave-sintered AZO targets, AZO thin films were prepared with various thicknesses on glass substrates at a temperature of 100-300°C by MSD or PLD using an AZO target sintered for about 30 min at a temperature of approximately 1250°C in an Ar gas or air atmosphere. For comparison, additional AZO thin films were prepared by MSD or PLD using an AZO target sintered for 5 h with a conventional furnace. The Al content (Al/(Al+Zn) atomic ratio) in sintered AZO targets was varied in the range from approximately 1.5 to 6 at.%. It was found that the obtainable resistivity of AZO thin films deposited using a millimeter-wave-sintered AZO target was less than or comparable to that produced in AZO films deposited using a furnace-sintered AZO target prepared with the same temperature and Al content. AZO thin films prepared with a thickness above 100 nm by PLD exhibited a low resistivity on the order of $2X10^{-4}$Ωcm. Using either type of target preparation, the obtainable resistivity of the deposited AZO films increased as the thickness was decreased; the thickness dependence of the obtainable resistivity in AZO thin films deposited using a millimeter-wave-sintered AZO target was comparable to that found in AZO films deposited using a furnace-sintered AZO target. Although the obtained resistivity and other properties in deposited AZO thin films were affected by the deposition method used, these properties were relatively independent of the sintering technique of the targets. It can be concluded that the newly developed energy saving millimeter-wave heating sintering technique is very well suited for producing sintered oxide targets.

**TF-ThP28 Study of Semiconductors III-V, IV-VI and II-VI Films Growth by PLD-M System**, ***M. González-Alcudia***, CICATA-IPN, México, *M. Meléndez-Lira*, CINVESTAV-IPN, México, *O. Calzadilla-Amaya*, Universidad Habana, Cuba, *M. Zapata-Torres*, CICATA-IPN, México

This research seeks to develop improved and innovative growth technique ( pulsed laser deposition modified: PLD-M ) for growing thin films based on III-V elements, such as Si and Ge, or II-VI elements, such CdS, CdTe and Tellurides. In addition, on advanced semiconductor alloy combinations such as CdTe/PbSnTe or other promising materials. Compared them with conventional growth of pulsed laser deposition for films, concerning microstructural properties. Films with different droplets morphology could be obtained under mild conditions. The films were characterized by X-ray diffraction (XRD) and SEM. The radius of droplets formed during single pulse irradiation is the rKH ≈ 0.05 - 5 μm. Our experiment shows that source materials and reaction temperature play important roles in forming the objecive products and controlling their morphologies. By this method, it is possible to prepare at low temperature, films with good chemical homogeneity.

**TF-ThP29 Mutual Inductance Characteristics of a Thin Film Planar Loop**, ***G.A. Topasna***, *D.M. Topasna, F.R. Powell*, Virginia Military Institute

We present a model of the mutual inductance of a thin film planar loop that is flux linked to a short straight wire. The mutual inductance is dependent on the geometry of the planar loop as well as its location relative to the wire. Our calculations provide closed-form and numerical solutions for various geometries. Calculations for the induced emf in the loop are compared to experimental measurements for various configurations.

**TF-ThP30 Room Temperature Photoluminescence from CdTe Nanocrystals Embedded within a $SiO_2$ Matrix Deposited on Silicon Employing Reactive RF Sputtering**, ***E. Mota-Pineda***, *M.A. Melendez-Lira*, CINVESTAV IPN Mexico

CdTe nanocrystals embedded in a SiO2 matrix were fabricated by radio frequency sputtering employing the texture of a SiO2 layer as template. The SiO2 film texture was controlled through the partial pressure of O2 (OPP) in the working atmosphere. The CdTe crystallinity is better for the samples synthesized on the rougher SiO2 films. Room temperature photoluminescence spectra showed a signal at 1.74 eV, related to the CdTe nanoparticles, for the samples that shown better crystallinity. Additional photoluminescence signals at 1.65 eV and 1.68 eV could indicate recombination process at the nanoparticles/matrix interface. These results indicate that the employed methodology allows to obtain room temperature light emitting CdTe nanoparticles in a single step. After thermal annealing all samples presented light emission related to quantum confinement; the photoluminescence emission can be controlled from 1.69 eV to 2.15 eV by an appropriate adjust of the OPP.

**TF-ThP31 The Influence of Pt Layers on the Corrosion Resistance of TiAl/TiAlN Multilayers**, ***M. Flores***, Universidad de Guadalajara, Mexico, *J. Avalos*, UAM-I, Mexico, *L. Huerta, R. Escamilla*, UNAM, Mexico

In this work we report the results of studies of the influence of Pt layers on the corrosion resistance of TiAL/TiALN multilayers deposited on 316L stainless steel. The multilayers were deposited by magnetron sputtering using targets of TiAL and Pt. The thickness of the Pt layers was from 50 nm to 500nm. The corrosion was studied using open circuit potential measurements and potentiodinamyc polarizations in ringer solutions. The results indicate that the corrosion resistance of TiAL/TiAlN multilayers is improved when Pt layers are deposited. The structure of multilayers was studied by means of XRD analysis. It was found that Pt layer has a strong influence on the structure of subsequent TiAlN layer. The corroded surface was studied by means of SEM and EDS. Pitting corrosion was observed in TiAl/AlTiN multilayers analyzed samples. RBS depth analysis was useful to determine the composition of each film and for modeling the interface characteristics through the heterostructure.

**TF-ThP32 Characterization of Metal Oxide Electrical Properties for Band Engineered Catalysis**, ***M.C. Kratzer***, *E.G. Seebauer*, University of Illinois at Urbana-Champaign

There is good reason to believe that the properties of semiconducting metal oxide catalysts can be improved when designed according to the principles of microelectronic devices. Since oxide semiconductors support space charge, it is possible for surface electronic properties to couple to bulk electronic properties. As a consequence, catalyst surface reactivity can be modified via electronic "band engineering," wherein the electronic properties of the underlying bulk alter the oxidation state of active sites at the free surface or modify the electric field in the space charge region adjacent to the surface. For example, hydroxyl group acidity on the $TiO_2$ surface can be tuned via the electron richness of the semiconductor, which can be manipulated via controlled doping. Current metal oxide catalyst synthesis methods do not permit doping with the requisite control for the band engineering approach, partly due to problems with measuring majority carrier type and concentration. Such determinations are difficult for metal oxides because the contacts employed for four-point-probe measurements need to obey Ohm's Law but, in practice, behave as diodes. The present work describes new methodology to solve this metrology problem, using $TiO_2$ as an example metal oxide. The approach involves synthesis of a thin film of the semiconductor on a silicon substrate by chemical vapor deposition or atomic layer deposition. A Schottky diode structure is then fabricated on the film to obtain the doping concentration from high frequency C-V measurements. For $TiO_2$, this approach has been implemented with aluminum contacts to the $TiO_2$ and InGa eutectic alloy contacts to the underlying silicon. The novelty of the structure lies in its compatibility with oxide semiconductors having widely varying doping levels, and the use of easily applied electrical contacts. Oxide thickness, uniformity, and crystal structure can be precisely tailored to suit the subsequent choice of reaction chemistry. A wide variety of fabrication issues have been characterized, including surface and interface preparation, contact metal type, and method of contact deposition. Detailed I-V measurements confirm diode-like behavior that is free from spurious artifacts and amenable to standard Mott-Schottky analysis. Values for the depletion width, barrier height, and series resistance are reported for the example case of $TiO_2$ synthesized from titanium tetraisopropoxide and $O_2$.

**TF-ThP33 Deposition and Characterization of Bi doped $Ge_2Sb_2Te_5$ Thin Films for Phase Change Random Access Memory Application,** ***J.H. Lee****, S.W. Ryu, Y.B. Ahn, C.S. Hwang, H.J. Kim*, Seoul National University, South Korea

Among the next-generation resistance based memories, PcRAM stores the digital data as different resistances of the phase change material between amorphous and crystalline phase. Although PcRAM has superior performances, there are still critical issues to be resolved i.e. reducing high amorphization current,[1] enhancing slow crystallization speed. $Ge_2Sb_2Te_5$ is the most well known phase change material for PRAM. Attempts has been made to improve the phase change properties of $Ge_2Sb_2Te_5$ by doping various elements and compounds such as N,[2] O[3] and SiO2.[4] In this report $Ge_2Sb_2Te_5$ was manipulated by doping Bi. Incorporation of Bi into $Ge_2Sb_2Te_5$ thin film was performed in two ways. First, by cosputtering $Bi_2Te_3$ and $Ge_2Sb_2Te_5$. Second, by sputtering $Ge_2Bi_2Te_5$ and $Ge_2Sb_2Te_5$ simultaneously. By cosputtering $Bi_2Te_3$ and $Ge_2Sb_2Te_5$, Bi was successfully incorporated into the lattice, which was confirmed by shifts in XRD peak positions compared to those of undoped $Ge_2Sb_2Te_5$. Cosputtering $Ge_2Bi_2Te_5$ and $Ge_2Sb_2Te_5$ guaranteed fixed atomic percentage of Ge and Te in the film with varying Bi contents. When the amorphous Bi doped $Ge_2Sb_2Te_5$ films crystallized by thermal annealing at about 150 °C, the resistivity of the film was reduced over 3 orders of magnitude, which was sufficient for device application. The Bi doped $Ge_2Sb_2Te_5$ films showed lower amorphization voltage without having to increase the crystalline resistance and demonstrated faster crystallization speed than those of $Ge_2Sb_2Te_5$.

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**TF-ThP34 Dynamic Scaling and Optical Study for Optimization of Thermally Evaporated Ag Thin Films on Glass,** ***J.R. Skuza****, C. Clavero, R.A. Lukaszew*, College of William & Mary

Noble metal (e.g. Ag, Au) thin films, also in nano-structured form, have recently been the subject of intense research for their possible applications (e.g. chemical and biological sensors, PV devices, etc.). Thermal evaporation is a suitable thin film deposition method that yields high quality Ag thin films. For example, reproducible production of thermally evaporated Ag thin films with tunable surface plasmon resonance wavelengths has been demonstrated with precise control of the deposition parameters.[1] Thus, understanding the growth dynamics of Ag thin films onto glass substrates by thermal evaporation and correlating these with optical properties is of great interest to link specific growth parameters to their desired properties. The surface of a film growing under non-equilibrium conditions often develops in agreement with the concept of dynamic scaling, where scaling exponents (e.g. $\alpha$, $\beta$) can be used as the spatial and temporal signatures of highly complex growth processes.[2,3] Here, we present a scaling analysis study on the surface morphology of thermally evaporated Ag thin films on glass substrates observed with atomic force microscopy. We find a dramatic change in the scaling exponents as a function of deposition rate, suggesting that there exists an optimum deposition rate in the range of studied values. This implies that there are competing mechanisms during the growth, such as the interaction energy of the adatoms and the substrate and their dynamics on the surface during the early stages of growth. Furthermore, these changes affect the microstructure and also have a profound effect on the optical properties, and in this case, we find that the optical properties of the Ag thin film approach bulk values at the optimum deposition rate.

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**TF-ThP35 Study of Slope Distribution with Mathematical Molding on Au(111) Thin Film Growth,** ***A. Gonzalez-Gonzalez****, J.L. Sacedon, E. Rodriguez-Cañas,* Instituto de Ciencia de Materiales de Madrid (CSIC), Spain*, J.A. Aznarez,* Instituto de Fisica Aplicada (CSIC), Spain*, E. Vasco*, Instituto de Ciencia de Materiales de Madrid (CSIC), Spain

In the present work two statistical methods of growth front analysis, the minimalist analysis and the mathematical molding, are compared. The minimalist method, previously developed,[1,2] is able to give a statically complete description of the surface, based in a linear limited sampling. It includes the capability to interpret the distribution of slopes at the border of surface protrusions. At difference the mathematical molding method allows to extend the sampling to all the image points and its handling is automatic. Applications of both methods on growth fronts of Au(111) thin films are presented. Thin Au films were thermally evaporated on Au epitaxied /mica substrates at 373K substrate temperature, resulting in a out of equilibrium mound growth (up to 60nm thick) on extended single crystalline plates. Atomic Force Microscopy (AFM) measurements were carried out to investigate the morphology of the films using high aspect ratio tips (nominal tip radius of 2 nm) to achieve high lateral resolution (estimated to be less than 3 nm). The molding algorithm is based on adaptive numerical interpolations of the AFM-measured surfaces by polynomial methods, the extended sampling results are coherent and can be interpreted with the set of parameters and shapes used in the minimalist method, allowing a better statistical determination. Using this method, we have investigated the evolution of the surface slopes with the film thickness and we were able to correlate slope distribution with terrace selected slope models and crystalline facets shaping the surface features.

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## Tribology Focus Topic
## Room: Hall D - Session TR-ThP

## Tribology Poster Session

**TR-ThP1 A Vacuum Tribometer to Depict Tribochemical Reactions of Lubricant Additives,** ***T. Le Mogne****, M.I. De Barros-Bouchet, J.M. Martin*, Ecole Centrale de Lyon -LTDS-, France

Today, it is well known that surface chemistry plays a key role in tribology and particularly in additives action under boundary lubrication. Tribochemical reactions are very difficult to predict because many parameters occur simultaneously in the tribological system. To simplify and to understand these phenomena, we have developed an analytical vacuum tribometer dedicated to the simulation of boundary lubrication conditions. A pin-on-flat tribometer is installed in a UHV chamber. Friction tests can be run in a wide range of surrounding partial pressures, typically from 10-8 hPa to atmospheric pressure. To study tribochemical reactions, we can introduce either pure gas or mixtures of gases (or vapours) into the chamber. Both pin and flat counterparts are introduced by a Fast Entry Load-Locks (FEL). The temperature of the flat specimen can be varied from room temperature up to 600°C. Before or after friction experiments, the two samples can be transferred without air exposure by using transfer mechanisms from the tribometry chamber into a preparation chamber and then to the analytical chamber. . This chamber is equipped with a hemispherical spectrometer build by ThermoFisher (220i). X-Ray Photoelectron Spectroscopy (XPS) can be done by using a focused monochromatic X-Ray source. A Field emission electron gun (FEG100) with a spot size lower than 1 μm allows Auger Electron Spectroscopy (AES). Ion gun (EXO5) is used for etching surfaces or for performing depth profiles. Imaging facilities are available by using a video camera for optical image, or a secondary electron detector coupled with the scanned FEG for Secondary Electron Microscopy (SEM). Chemical images can be obtained by Scanning Auger Microscopy (SAM) and XPS images by using dedicated lenses. The chemical reactivity of complex additive molecules with solid surfaces is simulated here by using small molecules with the same chemical function but with a lower molecular weight. Friction experiments are performed under variable partial pressures and at different temperatures. Mixtures of gases can be introduced to study synergistic or antagonist effects between chemical functions of additives. A residual gas analyser is installed on the vacuum chamber in order to control the purity of the gases and also to study any friction-induced outgases. We will present representative results with analyses performed inside and outside wear tracks to show chemical changes induced by tribochemical reactions.

**TR-ThP2 ToF-SIMS Investigations of Tribological Layers**, ***C. Bruening**, D. Lipinsky,* University of Muenster, Germany*, S. Neudörfer, G. Poll,* University of Hannover, Germany*, H.F. Arlinghaus*, University of Muenster, Germany

The formation of tribofilms plays a critical role in the longevity of automotive gears. A wide variety of anti-wear and extreme-pressure additives are commercially available for oil modification to build tribological layers and to reduce the friction between different friction partners and enhance the stability of the gear unit. Nevertheless, the behaviour of these layers under different stresses is not well understood. For this study, friction experiments under conditions typical for gear synchronisation were performed. Under standardized conditions on a test bench, rotating synchronisation rings fitted with typical friction linings consisting of brass, scatter sinter or carbon were decelerated on stainless steel cones. As lubricant, commercial gear oil was used, containing zinc dialkyldithiophosphate (ZDDP) and calcium sulfonate acting as AW/EP additive or as detergent, respectively. ToF-SIMS with its high surface sensitivity is well suited for these investigations. It was used to characterize the tribofilms generated by the wear process. Differences in contact pressures, relative velocities of the friction partners, and durations of stress led to the generation of different tribofilms, which is indicated by TOF-SIMS spectra, lateral distribution images, and depth profiles.

## Biological, Organic, and Soft Materials Focus Topic
## Room: 201 - Session BO+SS+AS-FrM

### Self Assembled Ultrathin Organic Interfaces
**Moderator:** S.L. McArthur, Swinburne University of Technology, Australia

8:40am **BO+SS+AS-FrM2 Photo-Patterned SAMs on Au(111) and SiO$_x$: An XPS Investigation**, ***A.M. Track**,* University of Graz, Austria*, A. Lex, T. Höfler, T. Griesser, P. Pacher, H.-G. Flesch,* Graz University of Technology, Austria*, G. Hlawacek,* University of Leoben, Austria*, R. Schenach, G. Trimmel,* Graz University of Technology, Austria*, W. Kern,* University of Leoben, Austria*, G. Koller, M.G. Ramsey*, University of Graz, Austria

Self-assembled monolayers (SAMs) can provide a simple, flexible, highly ordered and convenient system to tailor and functionalize surface and interface properties of metals, metal oxides and semiconductors. For instance a simple way to change the chemical reactivity of the substrates is to use organic photosensitive SAMs which will also allow patterning with UV illumination. We focus on the characterization of the reactions occurring in SAMs and thin interfacial layers using X-ray photoemission spectroscopy (XPS). To increase the contrast between the non-illuminated and illuminated SAMs (or thin films) we perform a selective post modification of the patterned films with organic reagents containing heteroatoms. The chemical differences of the structured film have been followed with spatially resolved XPS. Further chemical and structural information has been obtained with reflection absorption infrared spectroscopy (RAIRS), friction force microscopy (FFM), contact angle measurements and X-ray reflectivity (XRR). Two different types of photo-reactive functional groups have been investigated: a benzyl thiocaynate and a phenylester. First we present thin films of silanes on SiO$_x$, which bear the photoreactive benzyl thiocyanate (-SCN) unit. This photoisomerizes to the corresponding isothiocyanate (-NCS). The photoisomerization can be detected by a significant shift of the S2s core level. Additionally, we can prove the change of chemical reactivity due to the illumination via a post modification with fluorinated amines introduced in gas phase. Here more fluorine could be detected with the spatially resolved XPS on the illuminated areas of the sample.[1] In the second example the SiO$_x$ substrates are modified with photosensitive silanes of different chain length containing the phenylester group. The phenylester can undergo the Photo-Fries rearrangement upon UV illumination forming a hydroxyphenyl keton. The different chemical reactivity of these two groups is again shown with a selective post modification with, e.g., fluorinated acid chlorides. The corresponding reaction has again been followed by the appearance of the F1s signal only on the illuminated areas of the samples. Finally, results of investigations extended to patterned photo-reactive thiol-SAMs on Au(111) will be discussed.

[1] A. Lex et. al., Chem. Mater. 2008, 20, 2009-2015.

9:00am **BO+SS+AS-FrM3 Odd-Even Efect in Molecular Packing and Stability of ω-Biphenyl-Alkane-Selenol SAMs on Au(111)**, ***P. Cyganik**, K. Szelagowska-Kunstman,* Jagiellonian University, Poland*, M. Zharnikov,* Universität Heidelberg, Germany*, A. Terfort*, Marburg University, Germany

To fabricate aromatic self-assembled monolayers (SAMs) of practical importance for molecular electronics and other applications, high level of control over the SAMs properties should be achieved. In particular, besides monitoring the electronic properties, control of structure, i.e., crystallinity and defects, is an issue of equal importance. Our experimental approach to gain a general concept for the rational design of high-quality SAMs includes a systematic modification of the chemical composition of the SAM constituents and detailed investigation of the structure of the resulting films. Following this general idea, we studied the influence of the substitution of the headgroup atom (S versus Se, which binds SAMs constituent to the substrate) on the microscopic structure of hybrid aromatic-aliphatic SAMs formed on Au(111). The talk focuses on STM experiments[1] performed for the homologue series of BPnSe ($CH_3$-$(C_6H_4)_2$-$(CH_2)_n$-Se-, n =2-6) molecules. Obtained data are discussed and analysed in view of the spectroscopic results reported by us recently for these systems[2,3], as well as compared to the previously reported STM data[4,5] for the corresponding thiol-based analogues, i.e. BPnS/Au(111) . The main conclusions are: (1) higher structural quality of the Se based SAMs, (2) drastic changes in the BPnSe film structure depending on either odd or even value of the parameter n, accompanied by (3) the respective odd-even changes in their thermal stability.

[1] P. Cyganik et al. J. Phys. Chem. C, submited.

[2] A. Shaporenko et al. 2007 J. Am. Chem. Soc. 129, 2232.

[3] T. Weidner et al., J. Phys. Chem. C, submited.

[4] P. Cyganik et al. 2006 J. Am. Chem. Soc. 128, 13868.

[5] P. Cyganik et al. 2007 J. Phys. Chem. C. 111, 16909. .

9:40am **BO+SS+AS-FrM5 Unravelling Molecular Mechanism of Electron-Induced Cross-Linking in Aromatic SAMs**, ***A. Turchanin**,* University of Bielefeld, Germany*, D. Käfer,* Ruhr-University Bochum, Germany*, M. El-Desawy,* University of Bielefeld, Germany*, Ch. Wöll, G. Witte,* Ruhr-University Bochum, Germany*, A. Gölzhäuser*, University of Bielefeld, Germany

Irradiation of aromatic self-assembled monolayers (SAMs) with low energy electrons[1] or UV-light[2] results in a lateral cross-linking and the formation of aromatic carbon nanosheets with a thickness of only one molecule. These films possess a high mechanical stability that allows their separation from the substrate and fabrication of free standing membranes with a thickness of ~1nm[3] and exhibit further a remarkable thermal stability[4] sustaining temperatures above 1000 K. Because of the promising potential of these ultrathin membranes for various applications in nano-devices, the knowledge of their molecular microstructure and the mechanisms of cross-linking are of great interest. We have employed a variety of in situ spectroscopic techniques including X-ray photoelectron spectroscopy (XPS), near edge X-ray absorption fine structure spectroscopy (NEXAFS), thermal desorption spectroscopy (TDS), and UV photoelectron spectroscopy (UPS) to characterize the electron irradiation of 1,1'-biphenyl-4-thiol (BPT) SAMs on Au. Experimental data are further compared with quantum chemical calculations of the electronic structure of cross-linked species, which allowed the identification of distinct molecular species leading to the formation of carbon nanosheets upon electron irradiation of BPT SAMs. Molecular mechanisms of the electron induced changes in aromatic SAMs will be discussed.

[1] Geyer, W.; Stadler, V.; Eck, W.; Zharnikov, M.; Gölzhäuser, A.; Grunze, M.; Appl. Phys. Lett. 75 (1999) 2401;

[2] Turchanin, A.; Schnietz, M.; El-Desawy, M.; Solak, H. H.; David, C.; Gölzhäuser, A.; Small 3 (2007) 2114.;

[3] Eck, W.; Küller, A.; Grunze, M.; Völkel, B.; Gölzhäuser, A.; Adv. Mater. 17 (2005) 2583.;

[4] Turchanin, A.; El-Desawy, M.; Gölzhäuser, A.; Appl. Phys. Lett. 90 (2007) 053102.

10:20am **BO+SS+AS-FrM7 Self-Assembly of Methanethiol on the Reconstructed Au(111) Surface**, ***G. Nenchev**, B. Diaconescu,* University of New Hampshire*, F. Hagelberg,* East Tennessee State University*, K. Pohl*, University of New Hampshire

The molecular self-assembly of alkanethiols ($CH_3(CH_2)_{n-1}SH$) on Au(111) surface has been studied extensively in the last 20 years. Despite the abundance of experimental and theoretical data, the true nature of the processes involved in the monolayer formation is still not fully established. We will present a combined UHV VT-STM and DFT study of the adsorption of the simplest alkanethiol, methanethiol ($CH_3SH$), on the reconstructed Au(111) surface. Our findings challenge the established notion that methanethiol is too short to form ordered structures even at low temperature. At sub-monolayer coverage, dimer chains are resolved on the FCC areas of the reconstruction pattern. At higher coverage the monolayer evolves into two continuous self-assembled phases: a rectangular $c(4\sqrt{3} \times 2)$ phase, which coexists with the substrate reconstruction network, and a close-packed $p(\sqrt{3} \times \sqrt{3})R30°$ hexagonal phase. Our DFT calculation, which takes the reconstruction of the surface into account, confirms the non-dissociative character of the methanethiol adsorption and derives the bonding geometry of the molecular dimers - a sequence of shifted hollow-top and hollow-bridge bonding positions. The numerical calculation reveals that, in stark contrast to longer alkanethiols, at low temperature the self-assembly process of methanethiol is not driven by Van der Waals forces, but by a surface-mediated interaction. These novel results clearly demonstrate the unique nature of the methanethiol adsorption and self-assembly.

This work is supported by the National Science Foundation under Award #0425826 for the Center for High-Rate Nanomanufacturing and under Grant No. DMR-0134933. The computations are performed on the CRAY XT3 machine Sapphire at US Army/Engineer Research and Development Center (ERDC, Vicksburg, MS) in collaboration with Jackson State University, and supported by the DoD through Contract #W912HZ-06-C-005.

10:40am **BO+SS+AS-FrM8 Thermo Scientific Theta Probe : Measuring the Quality of Self-Assembled Monlayers on Gold**, ***P. Mack**,* Thermo Fisher Scientific, UK*, D.J. Graham,* Asemblon Inc*, J. Wolstenholme, R.G. White*, Thermo Fisher Scientific, UK

Self assembled monolayers (SAMs) are becoming increasingly important as a means to functionalise surfaces and to control surface properties or reactivity. The attributes of angle resolved X-ray photoelectron spectroscopy (ARXPS), such as surface specificity, chemical selectivity and non-destructive depth profiling, make it the ideal technique for characterising these layers. The Thermo Scientific Theta Probe was used to characterise the quality of self assembled monolayers on gold surfaces. For alkanethiol layers with high coverage, bonding was almost entirely via the thiol group (forming Au-S bonds). Mixed bonding modes were observed, however, with lower coverage, in agreement with a proposed mechanism for the formation of these films. The influence of the head group of the self-assembly precursor was investigated by analysing hydroxyalkanethiol and ethylene glycol monolayers.

11:00am **BO+SS+AS-FrM9 Morphology and Bonding in Alkene and Alkyne Based Monolayers Chemomechanically Formed on Si Surfaces***,* ***T.M. Willey****,* Lawrence Livermore National Laboratory*, M.V. Lee,* Materials Nanoarchitectonics, Japan*, J.R.I. Lee,* Lawrence Livermore National Laboratory*, M.R. Linford*, Brigham Young University

One of the most simple and economical methods for attaching and patterning alkenes or alkynes on silicon surfaces is through chemomechanical modification. Scribing the Si removes the oxide passivation layer, allowing the alkene or alkyne to chemisorb to the exposed and highly reactive Si surface. Near-edge X-ray Absorption Fine Structure (NEXAFS) spectroscopy reveals chemically homogeneous films with nearly monolayer coverage. Both alkene and alkyne precursors show no orientational order; however, more rigid perfluoronated molecules do have some incident angle dependence in NEXAFS resonances. Both alkenes and alkynes retain significant sp/sp$^2$ content. Hypothesized mechanisms of chemisorption are presented based on comparing the intensity of the sp/sp$^2$ features in the NEXAFS acquired from monolayers to measurements of precursor alkenes and alkynes in the gas-phase.

## 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 $C_{60}$ 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 nm$^2$ 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, $C_{60}$ molecules preferentially adsorb on the bare Cu regions on a partially N-covered grid surface. Subsequently a two-dimensional molecular nanomesh is formed after $C_{60}$ covers all the bare Cu regions. Further deposition leads to $C_{60}$ 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 $C_{60}$ growth. From there, the growth proceeds two-dimensionally until a single $C_{60}$ 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 $C_{60}$ overlayer with a nearest-neighbor $C_{60}$-$C_{60}$ distance of 1.02 nm. It is found that the interaction between $C_{60}$ and the c(2x2)-N surface is fairly weak, likely to be dominated by van der Waals forces, whereas the $C_{60}$-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 $2AB(ad)=A_2(ad)+B_2(ad)$ 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 $2NO(g)=N_2(g)+O_2(g)$, 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 $\Delta H^o$ to $2\Delta H^o$) strongly depends on the reaction exothermity. 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 micelles[1] to zeolite cavities[2] 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. Koblenz, 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

[1] Simpson, 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 um. 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 <100>. 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 µA to 24.7 µA 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$_2$ using BCl$_3$ 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 SiO$_2$ for reducing the gate-leakage current while maintaining the gate-dielectric capacitance. Therefore, there have been many studies on the dry etching of HfO$_2$ using halogen-based plasma etching for applications to MOSFET devices. A precise etch rate is required in the plasma etching for HfO$_2$ 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 HfO$_2$ and the under lying materials. These problems decrease the device performance. Atomic-layer etching (ALET) may be the most suitable method for etching HfO$_2$ in next-generation MOSFET devices because it may etch HfO$_2$ with no physical damage and with atomic-scale etch controllability. The etch characteristics of HfO$_2$ by ALET were investigated using a BCl$_3$./Ar neutral beam. The effect of ALET on surface modification and etch-depth control was also examined. Self-limited etching of HfO$_2$ could be obtained using BCl$_3$ ALET. This was attributed to the absorption of BCl$_3$ 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 HfO$_2$ 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.

## Plasma Science and Technology
## Room: 304 - Session PS1-FrM

## Plasma-Surface Interactions in Materials Processing II
## Moderator: T. Kropewnicki, Freescale Semiconductor

8:20am **PS1-FrM1 Effect of Annealing Temperature on the Response of $HfO_2$ to Vacuum Ultraviolet Radiation**, ***J.L. Shohet,*** *J.L. Lauer, G.S. Upadhyaya,* University of Wisconsin-Madison, *Y. Nishi*, Stanford University

The integration of high-k/metal gate stacks into CMOS technology poses several integration problems for the microelectronic industry. The metal gate electrode is often deposited on the high-k dielectric using plasma-sputter deposition; as a result, the high-k dielectric will be directly exposed to the plasma during metal-gate deposition. Plasma-induced charging damage from energetic electrons, ions, and photons has been found to degrade the electrical characteristics and reliability of the gate dielectric. In this work we use synchrotron radiation to determine the role that VUV radiation has in the production of electron-hole pairs created in HFO2 dielectrics on Si wafers with conductivities of 1000 and 4000 Ohm-cm. We determined the general valance band structure of the HfO2 dielectrics in the photon energy range of 5 and 30 eV. Since Argon is the feed gas most often used in plasma sputter deposition we determined the response of HfO2 films with thicknesses between 4 and 20 nm to the Ar-I emission line at 106.6 nm (11.6 eV), which is often the most intense emission line from an Ar plasma. After the dielectrics are irradiated with VUV, we measured the surface potential as a function of position across the irradiated region with a Kelvin probe. By measuring the surface potential for various thicknesses we are able to separately determine the density of surface and interface trapped charge. From the trapped charge densities we estimate the voltage across the dielectric during irradiation with the use of a mathematical model. By combining the current measurements with the estimated voltage across the dielectric we can determine the conductivity of the dielectric layers as a function of photon flux density. In addition, we determine the effect of annealing temperature of $HfO_2$ dielectrics as a function of total photon dose and compare the results to that of SiO2 films of similar thickness. There appears to be a correlation between the VUV-induced current density and annealing temperature with the total-induced charge measured after VUV irradiation.

Supported by the National Science Foundation under Grant Number DMR-0306582 and the Semiconductor Research Corporation under Contract Number 2008-KJ-1781. The Synchrotron Radiation Center is funded by the National Science Foundation under Grant Number DMR-0537588.
*G.S. Upadhyaya present address: Lam Research Corporation, Fremont, CA.

8:40am **PS1-FrM2 Response of BEOL Dielectrics to VUV Radiation**, ***J.L. Lauer***, *J.L. Shohet,* University of Wisconsin-Madison, *Y. Nishi*, Stanford University

Several integration challenges arise during plasma processing of back-end-of-line (BEOL) dielectrics with the scaling of interconnects from the 65 nm to the 45 nm technology node. This work focuses on the role that vacuum ultraviolet (VUV) radiation has in producing and/or mitigating damage to BEOL dielectrics during plasma processing. Vacuum ultraviolet (VUV) radiation with photons in the energy range of 5 to 30 eV produced by high-density plasmas in plasma-processing systems can cause degradation of electronic devices by producing changes in the optical, mechanical, chemical and electrical properties of dielectrics. In particular, VUV radiation is capable of creating electron-hole pairs within dielectrics. As a consequence of the increased conductivity, the dielectric layer acts as an antenna, being able to collect charges from the plasma which can cause charging damage. To determine how VUV can affect the electrical properties of dielectrics, we utilize synchrotron radiation incident on silicon wafers coated with dielectric layers which, in contrast to plasma exposure, has only photon flux incident on the dielectric surface. Measurements of the charging currents during VUV exposure appearing on dielectrics of various thickness and composition were made. In addition, the total induced charge that remains within the dielectric after VUV exposure was measured with a Kelvin probe. We show the effect VUV has on the induced trapped charge and conductivity of porous SiCOH films with dielectric constants between 2.55 and 3.00 for various film thicknesses. In addition, we compare the valence-band structure between 5 and 30 eV for different etch-stop dielectrics (SiN, SiC, oxygen-doped SiC, and nitrogen-doped SiC) and determine how the accumulation of space charge controls the conductivity of these films. These effects are compared with results obtained with $SiO_2$ to determine the potential integration challenges that these new dielectrics will pose in the future.

Work supported by the Semiconductor Research Corporation under Contract 2008-KJ-1781 and in part by NSF under grant DMR-0306582. The Synchrotron Radiation Center is funded by NSF under Grant Number DMR-0537588.

9:00am **PS1-FrM3 Mechanism of Plasma Ashing Damages on Porous SiOCH Films**, ***H. Yamamoto***, *K. Takeda, M. Sekine, M. Hori*, Nagoya University, Japan

The construction of integration process employing low dielectric constant (low-k) materials for interlayer dielectric is a key for the development of ULSI devices. Since the low-k films tend to be damaged during plasma processes, the damage free plasma processes are strongly required. Although many researchers have been studying on the plasma damage on the low-k films, there has been little in situ evaluation of plasma damages on the low-k films. The in situ evaluation is crucial for the clarification of damage generation mechanism because properties of damaged low-k films change when the low-k films are exposed to atmosphere. We built up an in situ measuring system to evaluate surface properties of the low-k films during plasma process. We investigated $H_2/N_2$ ashing plasma damages on porous SiOCH films and the correlation between the amount of damages and densities of radicals in the plasma which make large effects on low-k film properties during plasma process. The surface reaction was measured by using in situ Fourier transform infrared reflection absorption spectroscopy (FT-IR RAS) and spectroscopic ellipsometry. Absolute densities of H and N radicals were measured by vacuum ultraviolet absorption spectroscopy. The 100 MHz excited capacitively coupled plasma was used for the ashing process. The thickness of damaged layer was measured at a real time by the in situ spectroscopic ellipsometry and in situ FT-IR RAS during the ashing process. After the porous SiOCH were exposed to $H_2/N_2$ plasma at various flow rate ratios of $H_2/(H_2+N_2)$ for 60s, the thickness of damaged layer was monotonically increased with the flow rate ratio and reached the maximum of 33nm at that of 100%. H radical densities were increased with the flow rate ratio and had the maximum of $7.5\text{x}10^{11}\text{cm}^{-3}$ at that of 75 %, and then, decreased to $6.8\text{x}10^{11}\text{cm}^{-3}$ at that of 100%. N radical densities had the maximum of $9.5\text{x}10^{11}\text{cm}^{-3}$ at that of 25 %. The thickness of damaged layer agreed well with the H radical density in the region for 25% to 75%. Even though the H radical density decreased, the thickness of damage increased at the flow rate ratio of 100 %. On the basis of these results, we consider that damages on the porous SiOCH are determined by chemical reactions of H radicals which enhance the damage reaction and N radicals which have an effect of inhibition of the damages.

9:20am **PS1-FrM4 Surface Modifications of Ultralow Dielectric Constant Materials Exposed to Plasmas under Sidewall-like Conditions**, ***M.S. Kuo***, *G.S. Oehrlein*, University of Maryland at College Park

Fluorocarbon (FC)/Ar based capacitively coupled plasmas (CCP) are widely used for dielectric etch in back-end-of-line (BEOL) processes.

During formation of via/trench structures, highly polymerizing FC radicals deposit on via/trench sidewalls in parallel with ion-assisted etching of the dielectric. Since porous ultralow dielectric constant κ (ULK) dielectrics for 45 nm technologies or below are sensitive to plasma damage, FC thin film deposition on sidewalls is examined for its potential to protect ULK against plasma damage during subsequent process steps, e.g. photoresist ashing. For conditions where a small gap, high-aspect ratio structure in conjunction with blanket ULK films is used to simulate surface chemistry aspects of trench sidewalls we find that a thin (~1-3 nm) FC film deposits on the ULK surface and protects the ULK material against damage from other neutrals species, e.g. fluorine. The dependence of protection efficiency on FC film thickness and FC etching chemistry is discussed. The small gap geometry neglects the effect of scattered ions on ULK sidewalls, which potentially may produce surface modifications of actual ULK via/trench sidewalls. We attempted to address the effect of scattered ions, by examining ULK surface portions additionally bombarded by ions deflected at the edge of the gap structure. Fluorocarbon film deposition rates and composition were studied for these surface regions. The influence of these ULK surface modifications on ULK damage during photoresist mask stripping will be evaluated as a function of gap structure geometry, plasma chemistry and ion energy.

### 9:40am **PS1-FrM5 Degradation Mechanisms of Structure and k Value of Low-k Film by Plasma Irradiation**

***J. Chung**, S. Yasuhara,* Tohoku University, Japan, *K. Tajima, H. Yano, S. Kadomura, M. Yoshimaru, N. Matsunaga,* Semiconductor Technology Academic Research Center, Japan, *S. Samukawa*, Tohoku University, Japan

While the feature size of ultra-large-scale integrated circuits (ULSIs) has been shrinking, conventional Al/SiO$_2$ interconnects have been substituted by Cu/low-dielectric (low-k) film interconnects to reduce the resistance-capacitance (RC) delay and power consumption of the circuits . Since suitable Cu etching processes are not readily available, damascene processes have been developed for Cu/low-k interconnects. Plasma processes are extensively used for the etching of low-k films. However, since low-k films, such as porous silica films incorporated with methyl groups (SiOC films), are vulnerable to plasma irradiation, low-k films are severely damaged during plasma etching processes. During such processes, methyl groups are extracted from SiOC films due to ion, radical, and photon irradiation from plasma. As a result, the dielectric constant of SiOC films increases during plasma etching processes. We previously proposed a neutral beam process, in which the effects of photon irradiation from plasma can be eliminated, and using this process, we achieved low-damage etching/ashing of low-k films, which is not possible with the conventional plasma process. We speculated that the elimination of photon irradiation was attributed to the low-damage etching of low-k films. Still, the damage mechanism in low-k films during plasma etching has not been fully clarified. Further experiments are therefore needed to fully understand the degradation mechanism of structure and k value of low-k film and influences of ion, radical, and/or photon irradiation on the structure and k value of low-k film during the plasma etching processes. For these reasons, we precisely investigated the changes of structure (linear Si-O, Cage Si-O, Network Si-O, Si-CH$_3$/Si-O, Si-(CH$_3$)$_1$/Si-(CH$_3$)$_1$ ,and k value by ions, chemical reactions by radicals and ions, and photon irradiation on SiOC films during Ar, CF$_4$, O$_2$ and H$_2$ plasma irradiation. We found that the damage degree of low-k film depends on its structure components ratio.

### 10:00am **PS1-FrM6 Study of SiOxFy Passivation Layer Deposited in SiF$_4$/O$_2$ ICP Discharge used in Cryogenic Alternated Etching Processes**

***J. Pereira**, L.E. Pichon, R. Dussart, C.Y. Duluard, E.H. Oubensaid, H. Jiang, P. Lefaucheux,* GREMI, France, *M. Boufnichel,* ST Microelectronics, France, *P. Ranson*, GREMI, France

Silicon dry etching is widely used in microelectronics and microsystems industries in order to elaborate high aspect ratio structures [Micro-ElectroMechanical Systems (MEMS), Micro-OptoElectroMechanical systems (MOEMS) or integrated components]. In order to elaborate such deep structures, industry mainly uses the Bosch process, consisting of an alternation of isotropic etching (SF$_6$ plasma) and deposition (C$_4$F$_8$ polymerizing plasma) steps at ambient temperature. Even if this process can be well controlled, it presents many drawbacks such as sidewall roughness due to scalloping effect, or low etch rate. Thus, a new robust process used to form high aspect ratio structures into silicon bulk, called alternated cryogenic process (STiGer) is investigated.[1] Its principle consists of etching a silicon wafer cooled at cryogenic temperature (T~-80°C) by the alternation of isotropic (SF$_6$) etching steps and plasma deposition steps in SiF$_4$/O$_2$ gas mixture. The deposition step leads to the formation of a SiOxFy passivation layer used to protect the sidewalls and enhanced the anisotropic etching.[2] The formation of this passivation layer is not yet well understood, and its study is crucial for improving the cryogenic process. Moreover, fluorine-doped silicon dioxide films deposited by plasma have gained considerable importance for applications as low dielectric constant layers for reducing the capacitance between metallic lines in silicon based high-speed integrated circuits.[3] In this presentation, SiOxFy thin films deposited in ICP reactor are analysed in order to understand their formation and evaluate the effect of various parameters: SiF$_4$/O$_2$ gas mixture, substrate temperature, negative bias voltage or source power. The chemical structure and composition of the passivation layer is particularly studied. Fourier-Transformed InfraRed spectroscopy (FTIR) is used in order to determine the molecular groups constituting the coating and particularly the fluorine incorporation within the SiO$_2$ network and its consequences. Ellipsometric measurements give us informations on deposition rate and films characteristics such as refractive index, n.

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[2] X. Mellhaoui and al., J. Appl. Phys., 98 (2005) 104901.

[3] T. Homma, Mater. Sci. Eng., R Rep. 23 (1998) 243.

### 10:20am **PS1-FrM7 Anisotropic Fluorocarbon Plasma Etching of Si/SiGe Heterostructures and Induced Sidewall Damage**

***R. Ding**, M.G. Friesen, L.I. Klein, M.A. Eriksson, A.E. Wendt*, University of Wisconsin-Madison

Plasma etching is a critical tool in the fabrication of Si/SiGe heterostructure quantum devices, but it also presents challenges, including 1) control of etch profiles and 2) damage to etched feature sidewalls that affects device performance. 1) Fluorine-based plasma etching often results in device profiles with undercuts due to preferential etching of SiGe over silicon. A C4F8/N2/Ar etch plasma gas mixture introduced here has been successfully used to achieve straight sidewalls through heterostructure layers by formation of a fluorocarbon inhibitor film on feature sidewalls to prevent undercutting. 2) Chemical and structural changes in the semiconductor at feature sidewalls associated with plasma-surface interactions are considered damage, as they affect band structure and electrical conduction in the active region of the device. Here we report the results of experiments designed to better understand the mechanisms of plasma-induced sidewall damage in modulation-doped Si/SiGe heterostructures containing a two-dimensional electron gas (2DEG). Damage to straight wires was characterized both by the width of the non-conductive “sidewall depletion” region at the device sidewall and by the noise level factor, $\gamma_H$/N, determined from spectra of the low frequency noise. Observed increases in sidewall depletion width with increasing etch depth are tentatively attributed to the increase in total number of defects with increased plasma exposure time. Excess negative charge incorporated into the fluorocarbon inhibitor film could be another contributing factor. Other factors considered, including defects at the bottom of etched features as well as leakage current bypassing the wire, appear to contribute minimally. The noise level shows a minimum at an ion bombardment energy of ~100 eV, while the sidewall depletion width is independent of bias voltage, within experimental uncertainty. A proposed explanation of the noise trend involves two competing effects as ion energy increases: the increase in damage caused by each bombarding ion and the reduction in total ion dose due to shorter etch times and reduced ion flux to the sidewalls.

### 10:40am **PS1-FrM8 Influences of Electrical Characteristics in Carbon Nanotubes by Neutral Beam Irradiation**

***A. Wada**, Y. Sato,* Tohoku University, Japan, *M. Ishida, F. Nihey,* NEC Corporation, Japan, *K. Tohji, S. Samukawa*, Tohoku University, Japan

In an effort to realize carbon nanotube FET (CNT-FET), it is necessary to control electrical characteristics of grown CNTs by using plasma processes. However, the conventional plasma process induces severe damages into CNTs because charged particles and ultraviolet photons generate the defects in the CNTs. As a result, the CNT-FET could not be practically fabricated using conventional plasma processes. Here, we have proposed surface modification of CNTs by using our developed neutral beam to slove the problems and to control defects and electrical characteristics. Neutral beam can almost eliminate irradiation of charged particles and ultraviolet photons to CNTs. In this study, we irradiated Ar and N$_2$ time-modulated neutral beam (TM-NB) to single-walled carbon nanotubes (SWCNTs). Ultra violet-visible-near infrared (UV-Vis-NIR) spectroscopy was performed to understand the electrical characteristics SWCNTs before and after Ar and N$_2$ TM-NB irradiation. It was observed that Metal/Semiconductor peak intensity ratio was decreased after beam irradiation. This result means that the ratio of semiconductor nanotubes to metallic nanotubes increased after neutral beam irradiation. It is speculated that TM-NB mainly destroys metallic carbon nanotubes. Additionally, UV-Vis-NIR also confirmed that the band gap of SWCNTs was shifted to lower energy by the neutral beam irradiation. This result means band gap energy of SWCNTs can be controlled by the neutral beam irradiation. Based on these results, TM-NB could realize selective breaking of metallic carbon nanotubes and precise control of band gap in CNTs. As a result, we found that TM-NB could control electrical characteristics in CNT-FET.

11:00am **PS1-FrM9 Surface Modification of PTFE Surfaces with Post-Discharge RF Plasmas Operating at Low and Atmospheric Pressure,** ***N. Vandencasteele**, E. Carbone, F. Reniers*, Universite Libre de Bruxelles, Belgium

PTFE samples were exposed to post-discharges of RF plasma operating at low pressure (5 10-2 torr,pure O2) and at atmospheric pressure (Ar-O2). The plasma phase was characterized using optical emission spectrometry (OES). More specifically, the intensity of the O 777 nm line was chosen as a probe for the chemical reactivity of the plasma. The PTFE surface was characterized using monochromatized XPS, dynamic water contact angle, and atomic force microscopy. Depending on the power and treatment time, the surface energy could be either increased or decreased. At low power and/or treatment time, an increase in surface energy due to the grafting of oxygenated polar species is obtained. At high plasma power, a decrease in surface energy, leading, in some cases, to superhydrophobic surfaces is obtained. No oxygen is detected on such surfaces by XPS, and the superhydrophobic behaviour is attributed to an increase in roughness, as evidenced by AFM. By changing the position of the sample in the low pressure system, we could discriminate the role of the electrons, and the one of atomic oxygen. It is suggested that the increase in roughness is due to a chemical etching of the surface, initiated by high energy electrons, and terminated by the formation of gaseous products, CO and CO2, as detected by OES. A reaction mechanism is proposed. Interestingly, similar behaviours are observed using the low pressure system, and the atmospheric pressure system, in one particular geometry. The comparison between low pressure and high pressure results, on the same kind of sample, with the same type of plasma generation (RF mode) opens new routes for the understanding of surface reaction mechanisms at the atmospheric plasma – polymer interface.

This research is funded by the IAP "plasma surface interactions", from the Belgian Federal Government.

11:20am **PS1-FrM10 CoSi$_x$ Damage in Etching and Ashing Plasma,** ***K. Katahira**,* Sony Semiconductor Kyushu Corporation, Japan, *T. Tatsumi, S. Kobayashi, M. Fukasawa,* Sony Corp., Japan, *T. Takizawa, M. Isobe, S. Hamaguchi,* Osaka University, Japan, *K. Nagahata*, Sony Corp., Japan

Silicidation of the source/drain is required to produce high-speed CMOS devices, and suppressing the fluctuation of the contact resistance is one of the most important issues. In this study, we clarified the mechanism of fluctuation in contact resistance caused by plasma processes, and we vastly improved the controllability. The relationship between the plasma parameters and the contact resistance to CoSi$_x$ was investigated using a dual-frequency (27/2 MHz) CCP system. A SiO$_2$/SiN/CoSi$_x$ stacked sample with hole patterns was used. A CF$_4$ or CH$_3$F based plasma was used for SiN etching and O$_2$ or H$_2$/N$_2$ plasma was used for the subsequent ashing process. The thickness and composition of the damaged layer were analyzed using XPS, SIMS, and TEM. The ion energy distribution function and the ion penetration depth were calculated using a Monte-Carlo simulation, and a newly developed molecular dynamics (MD) simulation for a Si-O-C-F-H system, respectively. The resistance of the contact increased more when CH$_3$F was used than when CF$_4$ used, and a further increase was observed in a high V$_{dc}$ condition in CH$_3$F. We found that the resistance increase was caused by incident ions from the plasma. The mass number of dominant ions (CH$_2$F$^+$; m/e=33) in CH$_3$F plasma was much lower than that (CF$_3^+$; m/e=69) in CF$_4$ plasma. An MD simulation revealed that the dissociated C, H, and F species from CH$_2$F penetrate deeper than those from CF$_3$ due to the mass number difference of parent ions. Deeper damage caused by the ion penetration stimulates a deeper oxidation of CoSi$_x$ and raises the contact resistance. We also investigated the effect of the ashing process on the contact resistance. When using a high V$_{dc}$ condition during ashing, the contact resistance increased significantly. In particular, even in H$_2$/N$_2$ ashing, not using O$_2$, the contact resistance increased. When H$_2$/N$_2$ plasma, the damage of CoSi$_x$ was formed by deep H penetration. The damaged CoSi$_x$ layer can be readily oxidized during air exposure, resulting in the resistance increase. We observed that the contact resistance has a linear relationship with oxygen concentration in CoSi$_x$. Thus, precise control of the ion energy as well as proper selection of the ion species in the plasma process is indispensable in the fabricating next-generation devices.

## Plasma Science and Technology
## Room: 306 - Session PS2-FrM

### Plasma Processing for 3-D Integration, Photonics, Optoelectronics, and Memory Devices

**Moderator:** C.C. Hsu, National Taiwan University

8:20am **PS2-FrM1 Silicon Oxide Sidewall Passivation during HBr Inductively Coupled Plasma (ICP) Etching of InP and GaAs Materials for the Fabrication of Photonic Devices,** ***S. Bouchoule**, S. Guilet, L. Gatilova, G. Patriarche, L. Largeau,* LPN, CNRS, France, *P. Chabert*, LPTP, CNRS - Ecole Polytechnique, France

The ICP etching technique is now widely used for the anisotropic etching of III-V heterostructures, a key building-block for photonic devices. Chlorinated atmospheres are generally used for both InP and GaAs materials, with few studies devoted to HBr. In any case, very few studies exist on the understanding of the sidewall passivation mechanisms occurring during the etching of III-Vs. Using EDX-TEM ex-situ analysis, we have shown for the Cl2-H2 chemistry [JVSTB 26, 666 (2008)] that a silicon oxide layer acting as a lateral etch-inhibitor can build-up on the etched sidewalls of InP-based heterostructures, when a Si wafer is used as the sample tray. This configuration corresponds to most commercial ICP etch systems having an electrode diameter of 4-in or more, used to etch III-V samples of 2-in or less size. In this work, we have analyzed by ex-situ EDX-TEM the passivation layer deposited on the sidewalls of InP and GaAs pillars etched with HBr using a Si tray. A Si-rich layer can build-up on the etched sidewalls under low pressure and high ICP power conditions, leading to anisotropic profiles. The passivation mechanism resembles that identified in Si gate etching using Cl2-HBr-O2 plasmas, and we suggest that a minimum amount of oxygen should exist in the plasma for the passivation layer to build-up. OES measurements indeed showed that oxygen is present in the gas phase, even w/o intentional O2 addition. In our conditions (0.5 mT–1 mT pressure range and ~1000 W ICP power), high values of plasma potential (> 20V) and positive ion current (> 3 mA/cm2) are measured, and oxygen could come from the sputtering of either the Al2O3 ceramic inner parts or the passivated walls of the reactor. We identified that the walls state greatly influences the sidewall passivation process, indicating that the species desorbed from the conditioned walls play an important role. Moreover, we show that adding less than 10 % of O2 to the gas mixture can modify the passivation mechanism: it is strongly enhanced in the case of GaAs material, and the layer is changed from a Si-rich layer to a more stoechiometric SiO2 in any case. The InP and GaAs planar etch rate is also increased, to the benefit of selectivity against dielectric mask, indicating that the concentration of reactive radicals is modified by the addition of a small amount of O2 in HBr. Low loss laser ridge waveguides on InP(311)B substrate and AlGaAs/GaAs microcavities are demonstrated with the optimized process.

8:40am **PS2-FrM2 Low Bias Inductively Coupled Plasma Etching of CdHgTe in CH$_4$/H$_2$ Based Chemistry,** ***F. Boulard**, C. Cardinaud,* IMN CNRS France, *J. Baylet*, LETI-CEA, MINATEC France

CH$_4$/H$_2$ based dry etch chemistry is still under study for patterning of high aspect ratio trenches or holes in II-VI compound semiconductor cadmium mercury telluride (Cd$_x$Hg$_{1-x}$Te) used for high performance infrared detectors.[1] Since energetic ions bombardment induces electrical damages,[2] development of a gentle, low bias and chemistry assisted process is investigated. Plasma diagnostics and materials characterizations are developed to obtain a better description of etching fundamental mechanism. Inductively Coupled Plasma (ICP) reactor, allowing decoupling of plasma generation and substrate polarization, is used. Process parameters under study include gas mixture (using CH$_4$, H$_2$, N$_2$ and Ar), bias voltage, source power and substrate holder temperature. Experiments are carried out on alloys which composition varies from x=0.23 to 1. Langmuir probe and mass spectrometry measurements are used to correlate plasma modification induced by N$_2$ addition to the gas mixture with etched surface characteristics and etch rate. Etch product identification confirms the formation of TeH$_2$, while direct evidence of Cd(CH$_3$)$_2$, as proposed in the literature[3,4] is discussed. Post etch quasi in-situ X-ray photoelectron spectroscopy and spectroscopic ellipsometry suggest that etching occurs through a carbonaceous, Cd-rich and Hg-depleted layer. When the bias is significantly decreased to a value as low as 10V and the substrate holder temperature is raised, an average etch rate increase and a strong reduction of the extreme surface Cd/Hg ratio are observed, confirming an enhancement of chemically assisted elimination of Cd. The process developed offers smooth, mirror like, surface morphology and etch rate higher than 300nm.mn$^{-1}$ on $Cd_{0.23}Hg_{0.77}Te$.

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9:00am **PS2-FrM3 Characterisation of InP Ridge Sidewalls Patterned in Inductively Coupled Halogen Plasmas**, ***C. Cardinaud***, IMN-CNRS, France, *S. Bouchoule*, LPN-CNRS, France

High-aspect-ratio etching of InP-based heterostructures is a critical building block for photonic device fabrication. Indeed highly anisotropic profiles and smooth sidewalls free from undercuts or notches are required to minimize optical scattering losses. Recently it was shown that anisotropic etching can be obtained in Cl2-H2 and HBr inductively coupled plasmas (ICP), due to the passivation of the InP sidewalls by a Si-containing layer originating from the Si sample tray [JVSTB 26(2008)666]. This study is focused on the chemical characterisation by means of X-ray photoelectron spectroscopy of the bottom and sidewall surfaces of InP ridge patterns etched with Cl2-H2 and HBr chemistries. Anisotropic profiles are obtained for low pressure (<1mT), high ICP power (up to 1000W for HBr), H2 percentage (H2%) in the 35-45% range for the Cl2-H2 mixture, moderate dc bias (-140V), sample temperature of ~190°C. ICP etching results are compared to HCl wet etching, taken as reference. Surface chemistry at the pattern bottom can be summarized as follows. Etching in Cl2-H2 with a H2% ~36% gives a surface very close to HCl. Width of the P2p, In3d and In4d InP-bulk contributions are very close to the reference, this indicates that no other species than the oxide is present above the bulk material. The intensity ratios for In/P-bulk (0.9) In/P-oxide (0.6) point out that Cl2-H2 etching produces a slightly P-rich surface. In the case of HBr, the much larger width of the InP-bulk components suggests the occurrence of an additional species that could be amorphous InP. Moreover, an extra component is observed on the P2p spectrum at +0.8eV from that of InP-bulk. In the absence of Br from the surface, we suggest attribution to P-H species. Finally, the high In/P-bulk and In/P-oxide ratios, 4.3 and 3.9 respectively, clearly state that HBr produces an In-rich surface. Sidewall chemistry shows significant differences as compared to the bottom. For example in the case of Cl2-H2, the P2p, In3d and In4d InP-bulk contributions are about 1.5 times larger. Moreover the In/P ratio falls down to 0.4 and about 0.1 for In/P-bulk and In/P-oxide respectively. Opposite, the HCl etched sidewall is identical to the bottom (In/P-bulk = 0.9). For Cl2-H2 etching, this definitely points out a variation of composition in the top 10nm, with a decreasing In/P ratio from the "bulk" to the sidewall surface. Similar analysis are presently carried out on HBr and HBr-O2 etched samples.

9:20am **PS2-FrM4 The Plasma Polymerization of Novel Metal Containing Monomers Via Sublimation of the Precursor Materials**, ***J.O. Enlow***, UES, Inc., *H. Jiang*, Materials Sci. and Tech Applications, LLC, *J.T. Grant*, University of Dayton, *K.G. Eyink*, Air Force Research Laboratory, *W. Su*, AT&T Government Solutions, *A.M. Urbas*, *T.J. Bunning*, Air Force Research Laboratory

A flowing afterglow plasma reactor has been recently modified to incorporate a custom designed sublimation system for the fabrication of thin films from solid organic monomers. Some metal containing precursors such as ferrocene, as well as Cu, Fe, Mg, Ni, Pb and Zn phthalocyanines and porphorines have been successfully deposited. The optical properties of the films were investigated using variable angle spectroscopic ellipsometry and UV-Vis spectrometry, the chemical composition was determined using FT-IR and XPS and the morphology was examined using AFM and X-ray reflectivity. It was found that due to the incorporation of metal components, these films have relatively high indices of refraction when compared to conventional PECVD hydro-carbon films. Also, through the optimization of the deposition conditions original structural features were maintained in these highly crosslinked thin films. This study demonstrates that the use of sublimation opens up the PECVD technique to a wealth of new solid state and metal containing materials for the fabrication of novel optical and electronic thin films.

9:40am **PS2-FrM5 Advancement and Characterization of 3D TSV Etch Applications**, ***C. Rusu***, Lam Research **INVITED**

Implementation of TSV modules in production for 3DIC applications has become a technical and fundamental reality to contend with. Almost every semiconductor manufacturer is either directly working on TSV module design and development, or – if fabless, is working with partners for implementation of TSV modules. It is clear that CMOS Image Sensors (CIS) are leading the pack in implementation, with memory suppliers following closely. However, it is unclear at this time which memory segment will choose to implement TSV's first; DRAM or Flash, perhaps for reasons more related to economics than technology. This talk will primarily focus on the etch requirements for the TSV module. Etch challenges can vary widely with different applications, such as CIS, Memory, or Logic. In addition, TSV etch challenges vary for different integration schemes, such as via first, via middle, or via last. Therefore, it is without surprise that the TSV etch development tasks have been quite challenging, and existing etch equipment were not immediately applicable for TSV implementation. Recent development and upgrades have been made to address these market requirements, whether for silicon or glass substrates. We will show results of a flexible process system that can etch the multi-film stacks in addition to the deep silicon required to form TSVs. Substrates are patterned with either photoresist or dielectric hard mask, ranging from the micron-level minimum geometries to several tens of microns. TSV etch examples will be demonstrated addressing different integration requirements ranging from patterned photoresist directly on silicon, to patterned photoresist on multi-stack films replicating some of the layers that may exist on processed IC wafers.

10:20am **PS2-FrM7 Investigation of Bottom Profile Degradation Mechanism in Extremely High-Aspect-Ratio Feature Etching**, ***N. Negishi***, *M. Miyake*, *K. Yokogawa*, Hitachi, Ltd., Japan, *M. Oyama*, *T. Kanekiyo*, Hitachi High-Technologies Corporation, Japan, *M. Izawa*, Hitachi, Ltd., Japan

As the half-pitch of DRAM design rule advances beyond the 50 nm, precistion plasma etching will be required to realize extremely high aspect ratio feature of over 30. According to the shrinkage of pattern CD and narrowing pattern pitch size, many kinds of profile degradations that occur especially at around bottom area, such as, bottom distortion, twisting, shortage of bottom CD, have been observed. We assume that the mechanism of these etching profile degradations has closely connection with the combination of mask profile deformation, charge-up phenomenon, and the change of etch-front condition at bottom region. In order to diminish these profile degradations, we investigated the mechanism in terms of mask profile deformation effect with using ultra-high-frequency ECR (UHF-ECR) plasma etching system.[1] In this study, we used trench pattern to evaluate the degree of pattern deformation quantitatively as a function of pattern depth. Also, direct observation of etched pattern sidewall with using atomic-force-microscopy (AFM) was applied to clarify the relationship between bottom distortion and mask (necking) profile. The ratio of line width roughness (LWR) to line edge roughness (LER) that estimated from top view observation of etched sample after etch-back process decreased with increasing pattern depth and it means that pattern deformation becomes to 'wiggling' mode at deeper area. On the other hand, AFM observation of etched sidewall revealed that mask (necking) roughness is transferred to the bottom region and amplified drastically. As a result, we confirmed that using the mask of low degree of deformation is effective to diminish the bottom distortion.

(1) K. Yokogawa, N. Negishi, S. Yamamoto, K. Suzuki, and S. Tachi, 1997 Dry Process Symp., pp. 379-383.

10:40am **PS2-FrM8 Very Uniform and High Rate Si Etching Process in Advanced NLD Plasma**, ***Y. Morikawa***, *T. Murayama*, *K. Suu*, ULVAC, Inc., Japan

High-density of thru silicon via (TSV) is indispensable to the utilization and improvement in performance in 3D-LSI. Advanced high aspect ratio (A/R) TSV etching technologies are required for high-density TSV formation. We have developed a new etching system for TSV and MEMS application. This System provides combined plasma of magnetic neutral loop discharge (NLD) plasma and a sputtering system, which is named as NLD-Si.[1] For high rate silicone etching, it is very important to understand not only high density of the plasma generation but relation between fluorine diffusion (Z: distance of a wafer stage and NLD plasma) and the etching characteristic. In this study, a novel RF antenna 'multi slit rf antenna' has developed for the purpose of high rate etching. The number of slits of the antenna was increased from single line to three parallel lines to extend inductive coupling discharge region. Therefore, high-density generation of both of ion radicals is possible. Each slit interval is 25 cm. And, it is the feature that inductance (L) of this antenna is 0.52 uH and it is low L antenna. As a result of performing electron density measurement of the NLD plasma using this MS-RF Antenna, it succeeded in the high-density plasma production of $1x10^{12}$ / $cm^3$ by the process pressure of 2 Pa. Next, Si etching process development was performed using the Advanced NLD-Si etcher, which introduced a wafer stage elevator system. Si etching characteristics employing advanced NLD plasma were studied with respect to distance from an antenna. As a result, improvement in the etching rate of 2.5 times or more was realized as a result of optimization of the distance from NL. And, when process pressure and flow rate conditions were made to optimize, about 5 times the etch rate UP was achieved. Finally, the pattern of line width 1um attained the anisotropic etching of 8.5 um/min using Advanced NLD-Si etcher.

[1] Y. Morikawa, et al.; Thin Solid Films 515 (2007) 4918.

11:00am **PS2-FrM9 Fabrication of Very High Aspect Ratio Vertical Through Silicon Via by a Novel Multi-step Plasma Etching Technique**, ***P. Dixit***, Nanyang Technological University, Singapore, *R. Chatterjee*, Georgia Institute of Technology, *J. Miao*, Nanyang Technological University, Singapore, *R. Tummala*, Georgia Institute of Technology

In this paper, we present a novel multi-step etching technique to encounter the aspect ratio dependent etching (ARDE) characteristic of plasma etching process and to fabricate very high aspect ratio vertical through silicon vias. ARDE effect, which represents the reduction in etch rate at higher etching depth, is caused by the the depletion of etching radicals. The collisions of etching species with the outgoing reactions products and with the sidewalls, are also responsible for reduction in the etch rate. To maintain the constant etch rate and vertical sidewall profile, the depletion in the etching radicals should be compensated, which can be achieved by adding more etching radicals and plasma energy. To achieve this objective, we have proposed a multi-step etching technique, in which important DRIE parameters were gradually increased to maintain the constant etching flux . DRIE parameters, such as platen/coil power, SF6 and C4F8 flow rate, etching and passivation cycle duration, etc were increased in steps to provide 'additional etching species' needed at the bottom of the high aspect ratio etched features. At first, effect of individual parameters was investigated by varying a single parameter while keeping remaining parameters constant. 6 DRIE experiments were carried out to evaluate the effect of platen power on the etched profile (8, 10, 12, 14, 16 and 18 W). Similarly other experiments were performed to find the best parameter to overcome the depletion of etching radicals and to maintain the vertical etch profile. When the effect of individual parameters on etched profile was known, those parameters were chosen that gives the straight profile at relatively higher etch rate and with minimum undercut. Effect of platen power on controlling the perpendicularity of through-vias was found to be the most dominant among all parameters. A 200 nm aluminum layer was used as an anti-notching layer to prevent the lateral etching of vias at the bonding interface. Scanning electron microscope confirmed that the etching profile was completely vertical even at an etching depth as large as 510 micron. Using this technique, very high aspect ratio (>30), vertical through silicon vias having an opening dimension as small as 10 micron were fabricated. These DRIE etched through silicon vias were later electroplated to form copper interconnects, which are the most important building blocks for the next generation 3D stacking technology.

11:20am **PS2-FrM10 Through Silicon Via Etching for 3-D Interconnection using Pulse Inductively Coupled Plasma**, ***S.H. Lee***, *Y.D. Lim, W.J. Yoo*, Sungkyunkwan University, Korea, *O. Jung, S.C. Kim, H.C. Lee*, Dongbuhitek, Korea

Deep Silicon via etching technology is considered to be a critical and important factor to connect three-dimensional (3D) integrated-circuit system. In this process, the formation of deep Si via etching profiles is an important factor to accomplish filling of the highly conductive metal-materials and operating device in package level. We studied a non-Bosch type deep etching method using the pulse inductively coupled plasma (ICP) for the purpose of improving high aspect-ratio etching profile and reducing undercut at the entrance of the Si vias. We used an ICP etcher (ICP) in which wafer electrode is equipped with pulsing RF bias power which enabled the control of frequency, duty cycle and thereby was expected to affect ion acceleration onto the wafer surface and sidewall passivation of SiOxFy. SF6, O2, and Ar were used to accomplish deep non-Bosch –type Si etching for the pulse plasma discharge. To understand the effects of radicals in the plasma on the formation of etching profiles of deep Si vias, we monitored optical emission of radicals at 419.6 nm for Ar, 703.6 nm for F, and 777.0nm for O.

## Advanced Surface Engineering
## Room: 204 - Session SE+PS-FrM

### Pulsed Plasmas in Surface Engineering
### **Moderator:** A. Erdemir, Argonne National Laboratory

8:20am **SE+PS-FrM1 On the Plasma Parameters in the High Power Impulse Magnetron Sputtering Discharge (HiPIMS)**, ***J.T. Gudmundsson***, University of Iceland **INVITED**

The development of ionized physical vapor deposition (IPVD) was mainly driven by the formation of metal and nitride thin films into deep, narrow trenches and vias that are essential in modern microelectronics. More recently, the control of the ion energy and direction of the deposition species has proved to be an important physical tool in the growth process of new materials and new structures. Over the past few years, various ionized sputtering techniques have appeared that show a high degree of ionization of the sputtered atoms, in the range 50 - 90 %. This is often achieved by the application of a secondary discharge to a magnetron sputtering discharge, either inductively coupled plasma source (ICP-MS) or a microwave amplified magnetron sputtering[1]. High power impulse magnetron sputtering (HiPIMS) is a more recent sputtering technique that utilizes ionized physical vapor deposition (IPVD)[1],[2]. High density plasma is created by applying a high power pulse to a planar magnetron discharge. Measurements of the temporal and spatial behavior of the plasma parameters indicate peak electron density of the order of $10^{19}$ $m^{-3}$, that expands from the target with a fixed velocity that depends on the gas pressure[3]. The high electron density results in a high degree of ionization of the deposition material. Fractional ionization of the sputtered material has been measured to be over 90 %[2]. The ions are controllable with respect to energy and direction as they arrive to the growth surface. The spatial and temporal variation of the plasma parameters, electron density, electron energy, plasma potential and ion energy, in a HiPIMS discharge are reviewed. The plasma physics of the HiPIMS will be discussed as well as some of applications of the HiPIMS technique.

[1] U. Helmersson, M. Latteman, J. Bohlmark, A. P. Ehiasarian, and J. T. Gudmundsson, Ionized Physical Vapor Deposition (IPVD): A Review of Technology and Applications, Thin Solid Films 513 (2006) 1-24

[2] U. Helmersson, M. Lattemann, J. Alami, J. Bohlmark, A.P. Ehiasarian, and J.T. Gudmundsson, Proceedings of the 48th Annual Technical Conference of the Society of Vacuum Coaters, April 23-28, 2005, Denver, CO, USA, p.458

[3] J.T. Gudmundsson, J. Alami, and U. Helmersson, Spatial and temporal behavior of the plasma parameters in a pulsed magnetron discharge, Surf. Coat. Technol. 161 (2002) 249 .

9:00am **SE+PS-FrM3 Deposition of Metal Oxide Coatings using Reactive High Power Impulse Magnetron Sputtering**, ***E. Wallin***, *M. Aiempanakit*, Linköping University, Sweden, *T.I. Selinder, E. Coronel*, Sandvik Tooling, Sweden, *U. Helmersson*, Linköping University, Sweden

Metal oxides have been deposited using reactive high power impulse magnetron sputtering (HiPIMS) of metal targets in Ar/$O_2$ gas mixtures. The use of HiPIMS has in previous studies of deposition of alumina been shown to drastically influence the process characteristics compared to conventional reactive sputtering [Wallin and Helmersson, Thin Solid Films, in press]. Under suitable conditions, oxide formation on the target was found to be suppressed, and the hysteresis effect commonly observed as the gas flow is varied during conventional sputtering was reduced, or even completely eliminated, using HiPIMS. In the present work, these investigations are extended to a wider range of process parameters as well as to other material systems, including $CeO_2$, in order to better understand the reactive process. Based on this, reasons for the altered process characteristics will be discussed. Moreover, film properties of alumina deposited by this type of process have been investigated. α-alumina was found to form readily on both cemented carbide and Mo substrates at a temperature as low as 650 °C. α phase growth was retained over the studied range of substrate bias voltages (from floating potential to -100 V), while growth at lower temperatures resulted in the formation of γ-alumina at 575 °C and x-ray amorphous films at 500 °C or lower. The film microstructure was studied using electron microscopy techniques, revealing a plate-like structure of the α-alumina films with wider grains and a denser structure for higher bias values. Reasons for the phase composition and microstructure observed with different process parameters will be discussed together with possible pathways for further reduction of the α-alumina growth temperature and improvements of the microstructure.

9:20am **SE+PS-FrM4 A Mass/Energy Analysis of the Plasma during Modulated Pulse Power Sputtering**, ***W.D. Sproul***, Reactive Sputtering, Inc., *J. Lin, J.J. Moore, M. Hasheminiasari*, Colorado School of Mines, *R. Chistyakov, B. Abraham*, Zond, Inc./Zpulser, LLC

During modulated pulse power (MPP) sputtering, there are multiple steps within the overall pulse. Usually there are 3 steps, but there can be many more if needed. The first step is the application of a high voltage to the cathode that ignites a weakly ionized sputtering plasma. This weakly ionized plasma is allowed to stabilize in step 2, and then the voltage to the cathode is increase to transition the plasma into a strongly ionized plasma in step 3. This strongly ionized plasma is characterized by a significant increase in the current to the cathode accompanied with a moderate voltage increase. The overall power to the cathode is thus also greatly increased. At the substrate when a bias is used, there is also an increase in the substrate ion current density during step 3, and this ion current density increases as a function of the peak power. The deposition rate for the Cr films is a function of the peak power on the target, but there is a pronounced increase in the deposition rate when the peak power exceeds approximately 100 kW. In this study, a mass/energy analyzer was used to characterize the species in the plasma during the different steps of MPP sputtering of Cr films. Cr plus one ions were readily detected by the mass/energy analyzer in step 3 of the pulse, but it was more difficult to detect multiply charged Cr ions due to the location of the analyzer with respect to plasma and the target. It is possible that multiply ionized Cr ions are not detected due to charge exchange collisions in the plasma. The changes in the species in the plasma will be correlated with observed changes in the structure and properties of the Cr films deposited under different peak power conditions.

9:40am **SE+PS-FrM5 Process, Structure and Properties of Chromium and Chromium Nitride Coatings Synthesized using Modulated Pulse Power (MPP) Sputtering**, *J. Lin, Z. Wu,* Colorado School of Mines*, W.D. Sproul,* Reactive Sputtering, Inc.*, B. Mishra,* ***J.J. Moore****, M. Hasheminiasari,* Colorado School of Mines*, R. Chistyakov, B. Abraham*, Zond, Inc./Zpulser, LLC

Modulated pulse power (MPP) sputtering is a variation of high power pulse magnetron sputtering that overcomes the rate loss issue and achieves the enhanced plasma ionization through modulation of the pulse shape, intensity, and duration. In the current studies, Cr and CrN coatings were synthesized using MPP under different pulse durations and different combinations of the voltage rise and fall times, which were found to exhibit strong influence on the deposition parameters. It was found that the target power, voltage, current, and ion current density were increased with an increase in the long pulse durations and the voltage rise time. For Cr coating depositions, the MPP exhibits higher deposition rates than in the dc conditions when the average power is above 10-12 W/cm$^2$. A high deposition rate of 230 nm/min for the Cr coating deposition can be achieved with optimized pulsing parameters. The structure of the Cr and CrN coatings were characterized using x-ray diffraction (XRD), scanning electron microscopy (SEM) and transmission electron microscopy (TEM). The mechanical and tribological properties were measured by performing depth-sensing nanoindentation tests, micro-scratch tests and a ball-on-disc wear test in ambient atmosphere. It was found that the microstructure of the coatings changed from large columnar grains to dense and fine nano grains with an increase in the power and ion current densities on the target. A high hardness of 18 GPa has been achieved in Cr coatings deposited with an average power density of 21 W/cm$^2$ and an ion current density of 1.2 A/cm$^2$ on the target with a floating substrate bias.

10:00am **SE+PS-FrM6 Deposition Rate of High-Power-Pulse Magnetron Sputtering Processes**, ***J. Emmerlich****, S. Mráz, S. Konstantinidis,* RWTH Aachen University, Germany*, R. Snyders,* University of Mons, Belgium*, J.M. Schneider*, RWTH Aachen University, Germany **INVITED**

In high power pulsed magnetron sputtering (HPPMS), a large power density is applied giving rise to a high degree of ionization. From an application point of view, the major drawback of this technology is the considerably lower metal deposition rate as compared to DC magnetron sputtering. Using transport-of-ions-in-matter simulations (TRIM), it is shown that the apparently low deposition rate can be understood based on the non-linear energy dependence of the sputtering yields. The simulations are consistent with deposition-rate measurements on Cu films as well as with published deposition rate data for Ti [Konstantinidis et al., J. Appl. Phys. 99, 013307 (2006)]. TRIM simulations in combination with deposition rate experiments as a function of pulse width using Cu, W, and Ti as target materials reveal predominantly self-sputtering during Cu depositions. For W as well as Ti discharges, Ar contributes significantly more to sputtering, which may be explained by the low metal-self-sputtering yield. HPPMS deposition rates during reactive sputtering are reported to be comparable or even larger compared to DC magnetron sputtering rates [Wallin and Helmersson, Thin Solid Films in press]. Target erosion rate measurements for an HPPMS discharge exhibit two orders of magnitude larger erosion rates compared to DC magnetron sputtering.

10:40am **SE+PS-FrM8 Effects on Thin Film Growth Due to Anomalous Transport in High Power Impulse Magnetron Sputtering**, ***D. Lundin****, P. Larsson, E. Wallin,* Linköping University, Sweden*, M. Lattemann,* TU Darmstadt and Forschungszentrum Karlsruhe GmbH, Germany*, N. Brenning,* Royal Institute of Technology, Sweden*, U. Helmersson*, Linköping University, Sweden

In this study, the effect of a previously reported anomalous transport[1] on thin film growth in high power impulse magnetron sputtering (HiPIMS) has been investigated for the case of a planar circular magnetron. It was found that a large fraction of ions are transported radially outwards in the vicinity of the cathode, across the magnetic field lines, leading to enhanced deposition rates directly at the side of the cathode (on a substrate oriented perpendicular to the target surface). An important consequence of this type of mass transport parallel to the target surface is that the fraction of sputtered material reaching a substrate placed directly in front of the target is substantially lower in HiPIMS compared to conventional direct current magnetron sputtering (dcMS). This would help to explain the lower deposition rates generally observed for HiPIMS compared to dcMS. Moreover, time-averaged mass spectrometry measurements of the energy distribution of the cross-field transported ions were carried out. The measured distributions show a direction-dependent high-energy tail, which can be explained by an increase in the azimuthal force on the ions, exerting a volume force on the ions tangentially outwards from the circular race track region. These results are in agreement with predictions as well as recent modeling results of the anomalous transport mechanism.

[1] D. Lundin, U. Helmersson, S. Kirkpatrick, S. Rohde, and N. Brenning, Plasma Sources Sci. Technol. 17, 025007 (2008).

11:00am **SE+PS-FrM9 High Power Impulse Magnetron Sputtering of Ti-Si-C Multifunctional Thin Films**, ***M. Samuelsson***, Linköping University, Sweden*, H. Högberg, H. Ljungcrantz,* Impact Coatings, Sweden*, U. Helmersson*, Linköping University, Sweden

Nanocomposite Ti-Si-C thin films grown by dc-magnetron sputtering (dcMS) are interesting for many applications, such as in electrical contacts. This is due to a property envelope including low contact resistance, ductility and hardness that can be combined. Other areas of applications are also suggested, which call for increased possibility to design the material for specific needs. A promising deposition technique is high power impulse magnetron sputtering (HiPIMS), which offers a high degree of ionization of the sputtered material not found in conventional dc-magnetron sputtering. Growth from ions instead of neutrals is likely to further increase the possibility of designing the film microstructure and thereby the properties. In this study we have investigated sputtering from a $Ti_3SiC_2$ target by HiPIMS and compared the technique with dcMS. The techniques have been compared for different process pressures and substrate bias voltages using a pilot plant deposition system under production like conditions. The results show that the obtained HiPIMS growth rate was approximately 13% of that of dcMS for comparable average powers. Further studies employing SEM, TEM, XRD measurements, surface resistivity and film adhesion will be presented.

11:20am **SE+PS-FrM10 Modulated Pulse Power Deposition of Aluminum Oxide Nanometer Scale Multilayer Films**, ***R. Chistyakov***, Zond Inc.*, B. Abraham,* Zpulser LLC*, W.D. Sproul,* Reactive Sputtering, Inc.*, J.J. Moore, J. Lin*, Colorado School of Mines

Modulated pulse power (MPP) sputtering is a versatile high power pulse magnetron sputtering technique in which there can be multiple voltage steps within a pulse. Different levels of applied voltage in the same voltage pulse will generate different power levels for the magnetron discharge. Usually each pulse shape has a weakly ionized plasma (low power magnetron discharge) step that was generated first, and then the second stage that has a strongly ionized plasma (high power magnetron discharge) by applying a voltage increase to the cathode. These arbitrary voltage pulse shapes can be used within a given deposition run to form multilayer film structure. Therefore every layer can be sputtered with a different voltage pulse shape. In this study, two different voltage pulse shapes were selected. The first pulse had a shorter duration that the second pulse, but by varying the repetition rate the same average power could be delivered during the sputtering of each layer. The peak power applied to the plasma was greater during the second pulse, which meant that a greater amount of energy was applied to the process during the peak power phase of the second pulse. The difference in the applied energy between the two MPP pulse shapes was used during the reactive sputter deposit of aluminum oxide films . This two-pulse approach did produce a nanometer scale layering of the aluminum oxide coatings, which was observed in a scanning electron microscope. The thickness and structure of each nanometer scale layer was controlled by varying the output voltage pulse shape of the MPP plasma generator and deposition time. The layering of the aluminum oxide affected not only the structure of the films, but it also affected the mechanical properties of the films. The film structure, orientation, and mechanical properties were analyzed and measured, and the results of the film property measurements will be presented.

11:40am **SE+PS-FrM11 The Specification and Optimization of HIPIMS Power Supply Parameters**, *D. Ochs,* Huettinger Electronics GmbH, Germany*, P. Ozimek,* Huettinger Electronics Sp. z.o.o., Poland, ***A.G. Spencer***, Alacritas Consultancy Ltd., UK

HIPIMS is a rapidly emerging technique for surface modification. It is well know the improvements in surface properties that can be acheived (in particular in mechanical properties). What is less well known is how to specify and operate the HIPIMS power supply. There are many aspects of the HIPIMS power supply that need to be specified at time of purchase, and adjusted for process optimization (average power, pulse power, pulse frequency, pulse length). Usually HIPIMS users are upgrading from a sputtering or evaporation process. These new HIPIMS parameters are therefore unfamiliar. This paper details the effects of each of these parameters, gives examples, and guidance on specifying a HIPIMS power supply.

## 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 $O_3$ 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 $Fe^0$ Atoms, Clusters and Nanoparticles with $CCl_4$ 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 $Fe^0$ nanoparticles as an agent for the destruction of chlorinated hydrocarbons in environmental remediation applications. However, the fundamental reaction pathways for the interaction of nano-$Fe^0$ 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 $Fe^0$ atoms, clusters and nanoparticles are deposited into $CCl_4$ 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-$Fe_2O_3$/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-$Fe_2O_3$ (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 $SrTiO_3$ (001) Bulk Termination and 2x1 Reconstruction**, ***A.E. Becerra-Toledo***, *L.D. Marks*, Northwestern University

Strontium titanate, $SrTiO_3$, 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 $SrTiO_3$ 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 $SrTiO_3$ (001) surfaces. A repeated slab model was employed to study both a bulk-like $TiO_2$ 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 PBE[1] generalized gradient approximation (GGA) and the TPSS[2] meta-GGA. On the $TiO_2$-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 $H_2O$ molecule) much larger than that observed for the bulk $TiO_2$ 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).

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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 $TiO_2$(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 $O_2$ and H adatoms on reduced rutile $TiO_2$(110). We identified chemisorbed OH_O species as the initial intermediate that is produced by H transfer reactions to $O_2$ molecules, which concomitantly dissociate. Through further successive H transfer reactions, mediated by co-adsorbed water, the OH_O 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 $TiO_2$(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 $TiO_2$ surfaces has been intensely studied since the discovery of photoinduced splitting of water into hydrogen and oxygen on a rutile $TiO_2$ single crystal in 1972.[1] However, even though the anatase $TiO_2$ polymorph is more widely used as photocatalyst than rutile studies of the adsorption of water on well-defined anatase $TiO_2$ 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 $TiO_2$(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 $TiO_2$(001)-(4x1) surfaces were prepared: One by MOCVD growth on a lattice matched substrate [$SrTiO_3$(001)] and one by cleaning of a natural single crystal. Our results confirm that water dissociate on the anatase $TiO_2$(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.

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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 de-sorption 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.

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[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. Soukiassian***, 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) β2(2x4) Reconstruction*, M.H. Mignogna***, *K.A. Fichthorn*, The Pennsylvania State University

The GaAs (001) β2(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 calculations[1] have illuminated the mechanisms for recovering this reconstruction during growth. However, the KMC simulations are based on rates of processes that occur on perfect β2(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 β2(2x4) unit cells, but long-range disorder persists and a possible origin is out-of-phase β2(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 β2(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.

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[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 α2(2x4) and β2(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 α2(2x4) to be stable within an intermediate range of chemical potentials, giving way to the β2(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 α2(2x4) that posseses 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 $H_2O$. Energies and kinetics of adsorption and desorption of OH, H, and $H_2O$ are presented, which compares the stability of the HOOH/$H_2O$ vs the $H_2O$ 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.

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10:40am **SS+EM+NC-FrM8 Pit Nucleation in the Presence of (nx3) and β2(2x4) Surface Reconstructions on In$_{.81}$Ga$_{.19}$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 $(NH_4)_2S$ and ammonium hydroxide $NH_4OH$ 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 $(NH_4)_2S$ 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 $N_2$ 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 $Al_2O_3$, 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 $(NH_4)_2S$, 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 quantization[2] 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.

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