Biomaterials Plenary Session
Room: K - Session BP+NS-SuA

Nanoparticles: Advances in Fabrication, Characterization and Regulatory Challenges
Moderator: K.J. Wahl, Naval Research Laboratory, S. Zauscher, Duke University

3:00pm **BP+NS-SuA1 Using the Fabrication Technologies from the Microelectronics Industry to Address the Unmet Needs in Drug Delivery**, ***J.M. DeSimone***, UNC-Chapel Hill & NC State University **INVITED**

To translate promising molecular discoveries into benefits for patients, we are taking a pharmaco-engineering systems approach to develop the next generation of delivery systems with programmable multi-functional capability. Our laboratory has pioneered the development of a technique called **PRINT** (**P**article **R**eplication **i**n **N**on-wetting **T**emplates). PRINT is a remarkable top-down particle fabrication technique that has its roots in the fabrication techniques used in the microelectronics industry to make transistors. PRINT is a high resolution molding technique that allows the fabrication of precisely defined nano-particles with control over size, shape, deformability and surface chemistry. PRINT allows for the precise control over particle size (20 nm to >100 micron), particle shape (spheres, cylinders, discs, toroidal), particle composition (organic/inorganic, solid/porous), particle cargo (hydrophilic or hydrophobic therapeutics, biologicals, proteins, oligonucleotides, siRNA, imaging agents such as MR contrast agents, positron emitters), particle modulus (stiff, deformable) and particle surface properties (Avidin/biotin complexes, targeting peptides, antibodies, aptamers, cationic/anion charges, Stealth PEG chains).

3:40pm **BP+NS-SuA3 Designing Next Generation Nanoparticles for Self-Assembly and Reconfigurability**, ***S.C. Glotzer***, University of Michigan, Ann Arbor **INVITED**

Nanoparticles comprise a new generation of materials building blocks because of their diversity of shape, material and size, and because they can now be patterned and functionalized down to molecular scales with tailored and programmable interactions. The ability to create designer particles opens up exciting opportunities to create building blocks designed for self-assembly and even reconfigurability, in part through biomimicry. We show how, in the absence of a predictive theory, computer simulations play a critical role in elucidating how particle shape, interactions, and programmability can be exploited to achieve a high propensity for self-assembly into complex structures, including sheets, wires, helices, shells and other biomimetic structures.

4:20pm **BP+NS-SuA5 Nanotoxicology, Including Use of Nanomaterial Structure-Activity Relationships for Nanomaterial Safety Testing**, ***A.E. Nel***, University of California - Los Angeles **INVITED**

Because of the large number of new nanomaterials that are being produced, it is of increasing importance to develop a predictive platform for safety and risk assessment at the scale of technology expansion. The UC Center for the Environmental Impact of Nanotechnology (CEIN) is developing high throughput screening methods that incorporate relevant toxicological injury pathways that relate to the physicochemical properties of nanomaterials. I will discuss the emerging paradigms of toxicity that can be linked to the physicochemical properties of engineered nanoparticles with a view to outlining scientific principles that originate at the nano/bio interface and could determine which bio-physicochemical interactions occur and what leads to biocompatibility or toxicity. The major toxicological paradigm that has emerged from nanoparticle toxicity relates to the semiconductor, electronic, UV activation, and redox cycling chemistry of the particles, leading to biological hazard through the generation of oxygen radicals, electron-hole pairs and oxidant injury. It is possible to follow the oxygen radical generation and oxidant stress injury by abiotic methods as well as a set of hierarchical cellular responses that reflect protective, pro-inflammatory, mitochondrial damaging and pro-apoptotic outcomes. An oxidant injury pathway could translate into adaptive, pro-inflammatory or pro-apoptotic cellular effects in the lung, cardiovascular system, skin and the brain. Another paradigm relates to the ability of nanoparticles to absorb circulatory or cellular proteins as a function of particle size, surface area, functionalized surface groups, charge, hydrophobicity/hydrophilicity etc. This could induce protein unfolding, protein fibrillation, thiol crosslinking and loss of function, which could lead to neurotoxicity, loss of enzymatic activity, and generation of immunological responses. The thermodynamic properties and free surface energy of nanoparticles as a function of particle size, composition, phase and crystallinity could be responsible for particle dissolution in a biological environment, leading to the generation of cytotoxicity through the release of toxic ions or chemicals. ZnO will be discussed as an example of the latter category. I will demonstrate that it is possible to devise high content screening to capture these toxicological mechanisms, which can then be used to rank nanoparticle hazard and establish guidelines for safe design. If used as a preliminary screen for emerging nanomaterials, these predictive science-based approaches can help to determine which materials should undergo priority *in vivo* testing in the CEIN environmental mesocosms. I will also briefly discuss how these principles can be applied to toxicity testing and safe design of therapeutic nanoparticles.

Applied Surface Science
Room: C2 - Session AS+EM+MS+TF-MoM

Spectroscopic Ellipsometry I
Moderator: M.S. Wagner, Proctor and Gamble

8:20am **AS+EM+MS+TF-MoM1 Optical Properties of Bulk GaSe and InSe Single Crystals**, ***S.G. Choi***, National Renewable Energy Laboratory, *C. Martinez-Tomas, V. Munoz Sanjose,* Universitat de Valencia, Spain, *D.H. Levi*, National Renewable Energy Laboratory

III-VI compounds generally crystallize in layered-structures characterized by strong covalent interactions *within* the layers but weak Van der Waals binding *between* the layers. This unique structural characteristic has made III-VI compounds attractive for their potential applications in nonlinear optics. Among these compounds, in particular, InSe has been considered as a promising candidate for thin film photovoltaic (PV) material owing to its energy bandgap, optical and transport properties. Recently, high-quality epitaxial InSe thin films have been grown on GaSe substrates, and PV device structures containing *n*-InSe and *p*-GaSe have been successfully fabricated [1].

In order to design and optimize a high-performance PV device structure, knowledge of optical properties of constituent materials over a wide spectral range is required. However, large discrepancies were found in the properties of GaSe and InSe available in the literature, which have been measured mostly by reflectance methods with the Kramers-Kronig transformation employed to obtain the dielectric functions. Here, we present ellipsometrically determined pseudodielectric function $\langle\varepsilon\rangle=\langle\varepsilon_1\rangle+i\langle\varepsilon_2\rangle$ spectra from 0.73 to 6.45 eV of bulk GaSe (ε-phase) and InSe (γ-phase) single-crystals grown by a vertical Bridgman method. The surfaces with minimum overlayers were obtained by peeling off the top few layers from the sample surface and ellipsometric measurements were immediately followed under flowing N_2 environment, which yields good approximations to the intrinsic dielectric responses. The measured spectra exhibited a number of interband-transition critical-point structures, and their energy values were obtained precisely from numerically calculated second-energy-derivatives of $\langle\varepsilon\rangle$ assuming the parabolic-band critical-point model.

Data obtained in this work can be used to model PV device structures utilizing GaSe and InSe, and the critical-point energies determined will be useful for theoreticians to perform fine band structure calculations of III-VI compounds.

The work done at Universitat de València was supported in part by the Spanish Project MAT2007-06841. This abstract is subject to U.S. government rights.

[1] J.F. Sánchez-Royo, J. Appl. Phys. 90, 2818 (2001).

8:40am **AS+EM+MS+TF-MoM2 Ellipsometric Porosimetry for the Microstructure Characterization of Plasma-Deposited SiO_2-Like Films**, ***M. Creatore***, *N.M. Terlinden, G. Aresta, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

SiO_2 layers have been deposited from Ar/O_2/hexamethyldisiloxane mixtures in a remote expanding thermal plasma setup enabling a good control of both the ion flux (by changing the deposition chemistry and the arc plasma parameters) as well as the ion energy. This latter is achieved by an additional rf substrate biasing or a tailored ion biasing technique, i.e. a low frequency pulse-shaped bias. The role of the ion energy and ion-to-growth flux ratio on the film microstructure and densification at low substrate temperature (100ºC) has been investigated by means of ellipsometric porosimetry. This technique monitors the refractive index change due to the adsorption (and desorption) of ethanol vapors in the volume of macro-meso-micro pores in the SiO_2 layer. From the analysis of the adsorption isotherm and the presence of hysteresis during the desorption step as a function of the equilibrium partial pressure, the open porosity in the layer can be determined. It is found that both biasing techniques lead to densification of the deposited layer, which experiences a transition from micro-/ mesoporosity to microporosity and eventually non-porosity, as function of the increasing ion energy. Although both biasing techniques lead to a comparable critical ion energy value per deposited SiO_2 unit (about 100 eV), the ion-to-growth flux ratio and ion energy are not found to be interchangeable parameters. In fact, in the case of the rf bias, the meso- and large micropores are first affected leading to a quantitative decrease of porosity, i.e. from 11% to 3% at an ion energy less than 20 eV. A further increase in ion energy eventually reduces the presence of smaller micropores leading to non porous films at energy of 45 eV. When the pulse-shaped biasing technique is adopted, the micro- and mesopores are simultaneously affected over the whole range of available ion energy, leading to a non porous layer only at very high energy values, i.e. 240 eV. This difference is attributed to the increasing ion-to-growth flux ratio accompanying the rf biasing, as a consequence of the rf plasma generation in front of the substrate.

9:00am **AS+EM+MS+TF-MoM3 Industrial Applications of Spectroscopic Ellipsometry**, ***J.A. Woollam***, J.A. Woollam Company, Inc., *J.N. Hilfiker, P. He*, J.A. Woollam Company Inc. **INVITED**

Spectroscopic Ellipsometry (SE) has been used for decades for basic research on surfaces and thin films. Hundreds of articles, review papers, and books describe SE use in physics, chemistry and surface and materials engineering. Far less is available describing industrial applications because companies gain competitive advantage using SE and are not motivated to publish.

Without revealing anyone's proprietary information, this talk reviews examples of SE use in industry. This involves both production quality control (QC), and product development. Best known is SE for QC in integrated circuit manufacturing. Others include integrated circuit critical dimension (CD) metrology, read-write heads, display technologies, optoelectronics, photovoltaics (crystalline and thin film), optical coatings, web-coaters, wear surfaces, and protective coatings. Industrial SE applications include ex-situ, in-situ, and in-line metrology.

9:40am **AS+EM+MS+TF-MoM5 Spectroscopic Ellipsometry Studies of Sputtered Vanadium Oxide Thin Films**, ***N.J. Podraza***, *B.D. Gauntt, M.A. Motyka, E.C. Dickey, 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. However, vanadium can adopt many different oxidation states, yielding a number of stable metal oxides, which can lead to difficulties in reliable and consistent device fabrication. In this work, VO_x thin films were fabricated via pulsed-DC magnetron sputtering in an argon and oxygen atmosphere under variable total pressure and oxygen-to-argon ratio deposition conditions in order to investigate the variability in desired material properties. In situ real time spectroscopic ellipsometry (RTSE) has been applied to stuffy films prepared under variable deposition conditions in order to evaluate the microstructural evolution of VO_x during film growth and changes occurring to the surface and bulk material upon initial exposure to atmosphere. These films were characterized ex situ using a number of complementary techniques including, Rutherford backscattering spectroscopy (RBS) in order to obtain the oxygen content, x; transmission electron microscopy (TEM) to determine film crystallinity; glancing incidence X-ray diffraction (GIXRD) was used to ensure localized measurements from the TEM were representative of the entire film; and I-V curve measurements as a function of temperature were used to determine the film resistivity and TCR. By varying deposition conditions, the film resistivity was varied over seven orders of magnitude from $\sim 10^{-3}$ to 10^4 Ω-cm and the TCR spanned from -0.1 to -3.5 %/K. The growth evolution, complex dielectric function spectra ($\varepsilon = \varepsilon_1 + i\varepsilon_2$), and structure are correlated to these electrical properties. Films produced at low oxygen-to-argon ratios exhibit nanocrystalline V, V_2O, and VO phase material dependent on the specific deposition conditions, while films produced at higher oxygen-to argon ratios are amorphous. In both the nanocrystalline and amorphous phases, features in e obtained from spectroscopic ellipsometry have been shown to correlate with the oxygen content and resistivity and RTSE studies have been used to monitor changes occurring at the film / ambient interface after the vanadium oxide is exposed to air. This array of techniques were used to establish the roles deposition parameters play in the final structure and composition of each film, as well as to determine the resulting effects of these characteristics on the electronic transport and optical properties.

10:00am **AS+EM+MS+TF-MoM6 Real Time Spectroscopic Ellipsometry Studies of Si:H and Ge:H Thin Films for Microbolometer Applications**, ***D. Saint John***, *E.C. Dickey, N.J. Podraza*, The Pennsylvania State University

Thin film hydrogenated silicon (Si:H) and germanium (Ge:H) have been of wide interest as thin film semiconducting materials, and are now of growing interest for use in infrared sensing uncooled microbolometers, although the impact of the growth evolution and structure on device performance is only beginning to be determined. Ideal properties for incorporation of these layers in microbolometers include: a high temperature coefficient of resistance (TCR); controllable resistivity (ρ); low 1/f noise within frequencies of interest; and process compatibility with standard IC fabrication. In this work, n- and p-type doped Si:H and undoped Ge:H thin films have been prepared by plasma enhanced chemical vapor deposition (PECVD) with resulting resistivities ranging from 1.5 to 2500 Ω cm and TCR ranging from –0.8 to –4.0 %/K and studied using real time spectroscopic ellipsometry (RTSE). These films, monitored in situ during growth by RTSE, have been shown to exhibit changes in microstructure as a function of deposition conditions. For example, films prepared at low hydrogen dilution may remain amorphous throughout growth (a-Si:H), while films prepared at higher dilution may initially grow as amorphous until a bulk layer thickness where microcrystallites nucleate and eventually coalesce into a single-phase microcrystalline layer (μc-Si:H). A combination of in-situ RTSE, transmission electron microscopy (TEM), and electrical measurements (ρ, TCR, 1/f noise) have been used to study the effects of deposition conditions on the resulting microstructure during film growth and the dependence of the electrical properties on this microstructure. Studies of p-type a-Si:H have shown that both TCR and ρ increase with hydrogen dilution for fixed doping gas-to-silane ratio, which suggests that optimizing the TCR for a film of a given resistivity may potentially be obtained by varying both the hydrogen and doping gas dilutions. n-type a-Si:H and mc-Si:H films were evaluated in order to quantify changes in TCR and r resulting from microstructural differences (a-Si:H: ρ= 250 Ω cm, TCR = –3.8 %/K; μc-Si:H: ρ = 1.5 Ω cm, TCR = –0.8 %/K). Growth evolution studies of undoped Ge:H films prepared under variable hydrogen dilution conditions show transitions from amorphous to microcrystalline material at higher hydrogen dilution and relatively high TCR values ranging from –2.2 to –3.6 %/K as dilution is increased within the amorphous growth regime.

10:40am **AS+EM+MS+TF-MoM8 Non-destructive Determination of Spatial Distributions of Free-Charge-Carriers in Low Doped Semiconductors using THz Ellipsometry**, ***T. Hofmann***, University of Nebraska-Lincoln, *C.M. Herzinger*, J. A. Woollam Co. Inc., *M. Schubert*, University of Nebraska - Lincoln

The non-contact and non-destructive optical determination of spatial distributions of free-charge-carriers in low doped semiconductor homo- and heterojunctions addresses fundamental physical properties of device related structures. However, the optical characterization of low density free-charge-carriers, particularly for hole densities with their intrinsically lower mobility parameters than electron densities is very challenging. For low carrier densities the plasma frequencies are located at within the terahertz (THz) spectral region and measurements of plasma frequency properties in a at THz frequencies have been used for the determination of free-charge-carrier properties in single crystals (e.g. [1,2]). The characterization of free-charge-carrier properties in low-doped homo- and heterostructures remains a challenge.

Here we report on the non-invasive optical measurement of hole diffusion profile in a p-p$^+$ Silicon homojunction by spectroscopic ellipsometry in the terahertz (0.2 to 1.5 THz) and mid-infrared (9 to 50 THz) spectral regions. In the terahertz region a surface guided wave resonance with transverse-electrical polarization is observed at the boundary of the p-p$^+$ homojunction, and which is found to be extremely sensitive to the low-doped *p*-type carrier concentration as well as to the hole diffusion profile within the p-p$^+$ homojunction. Effective mass approximations allow determination of homojunction hole concentrations as p=2.9x10^{15} cm^{-3}, p^+=5.6x10^{18} cm^{-3}, and diffusion time constant D_t = 7.7x10^{-3} μm^2, in agreement with previous electrical investigations.

[1] D. Grischkowsky, Soren Keiding, Martin van Exter, and Ch. Fattinger, J. Opt. Soc. Am. B **7**, 2006 (1990).

[2] M. Herrmann, M. Tani, K. Sakai, and R. Fukasawa, J. Appl. Phys. **91**, 1247 (2002).

11:00am **AS+EM+MS+TF-MoM9 Ellipsometric Depth Profiling of Polymer-Blend Films for Organic Electronics and Photovoltaics**, ***L.J. Richter***, *D.S. Germack, D.M. DeLongchamp, D.A. Fischer, V.M. Prabhu, D.J. Gundlach,* National Institute of Standards and Technology, *J.E. Anthony,* University of Kentucky, *N. Shin, D. Yoon*, Seoul National University, Korea

Interest has emerged in the development of devices based on organic materials and low energy, low cost, roll-to-roll fabrication techniques. Two specific target applications have received particular attention: organic transistors to enable macroelectronics (large area displays, RFID tags, etc.) and organic photovoltaics. Common to both applications is the development of optimal inks: for macroelectronics, small crystallizable molecules in an inert polymer binder, for photovoltaics, fullerene based acceptors blended in an active polymer donor. Critical to a proper understanding of the device performance is an understanding of the vertical profile of the fabricated film. For thin film transistors, segregation of the small molecule semiconductor to the interfaces is essential. For PV, segregation of the fullerene can be both advantageous (if at the cathode) and deleterious (if at the anode). Spectroscopic ellipsometry studies of the vertical profile are daunting, as the systems are in general anisotropic with individual component spectra that are strongly dependent on the local order. We present SE studies of both TFTs and OPV devices using a multiple sample approach to remove correlations in the resultant models. The optical depth profiles are compared to both NEXAFS studies of the interface composition and neutron reflectivity studies of similar processed films. We find good agreement between the SE and less model dependent techniques. The studies illuminate general principles of the influence of interfacial free energy on the resultant segregation of the species.

11:20am **AS+EM+MS+TF-MoM10 Thickness Variations Determined by Spectroscopic Ellipsometry in Organometallic Chemical Vapor Deposition: Connection to Growth Processes**, ***X. Liu***, *D.E. Aspnes*, North Carolina State University

Lateral thickness variations are commonly observed for films deposited by organometallic chemical vapor deposition (OMCVD). The variations are typically systematic near boundaries between growth and adjacent surfaces, for example masks. We use spectroscopic ellipsometry to study thickness variations for the heteroepitaxy of GaP by OMCVD on (001) GaAs, thermally generated SiO_2, (001) Si, and nanoscopically roughened Si surfaces using trimethylgallium (TMG) and phosphine (PH_3) sources, showing that the variations provide information about details of OMCVD growth that would be difficult to obtain in any other way. Our reference surface is the polycrystalline GaP inadvertently deposited on the Mo susceptor that surrounds the 2 in. wafers. We find that the thicknesses of the deposited GaP films increase or decrease accurately exponentially toward the edge. Using an analytic Green-function approach based on the one-dimensional diffusion equation, we show that for our growth conditions (4 Torr chamber pressure), the exponential thickness variations are due to differences in chemical reactivities of the various surfaces, especially on the different catalytic effects that they exert on PH_3 decomposition. The results show directly that different parts of the surface, including the susceptor, are in constant contact with each other through lateral gas-phase diffusion. The data are explained by assuming that growth occurs via a precursor that is formed by heterogeneous catalysis, largely desorbs, and involves both Ga and P, for example the H-P=Ga-CH_3 dimer adduct. To distinguish this process from selective area growth (SAG), which takes place with a similar configuration, we also solve the SAG problem analytically, in this case using a conformal map. For SAG the thickness near mask edges is found to vary as $r^{-1/2}$, where *r* is the lateral distance away from the edge. The distinctive differences in these thickness dependences indicate that SAG growth occurs via a different mechanism.

11:40am **AS+EM+MS+TF-MoM11 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 was measured in-situ with the optical technique Reflection Anisotropy Spectroscopy (RAS).

The ion induced nanopatterning was done with 2 keV Ar ions with a flux of a few mA/cm2 in a temperature range of 300 - 420K. With RAS, a periodicity of ripples above 200 nm is measured by a shift in photon energy of the plasmon resonance. Features with a smaller periodicity show a plasmon resonance around 3.65 eV. For very grazing incidence sputtering, 80o 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 70o 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 roughening of the surface perpendicular to the direction of the ion beam in one direction suffices to describe the measured optical data. The evolution of the rms, wavelength and wavelength distribution of the ion induced nanoripples is obtained from the in-situ measurements. For a polar angle of the ion beam of 61o we find that also the roughening in the direction along the nanorippels has to be taken into account to describe the optical spectra.

Biomaterial Interfaces
Room: K - Session BI+NS-MoM

Nanoparticles and Self Assembly
Moderator: A. Chilkoti, Duke University, V. Perez-Luna, Illinois Institute of Technology

8:20am **BI+NS-MoM1 Self-assembling and Biofunctionalization of Plasmonic Gallium and Gold Nanoparticles on Semiconductors for Label Free Bio- and Chemo-sensing***, M. Losurdo,* IMIP-CNR, Italy*, P.C. Wu,* Duke University*, G.V. Bianco, M. Giangregorio,* IMIP-CNR, Italy*, T.H. Kim,* Duke University*, G. Bruno,* IMIP-CNR, Italy*, **A.S. Brown***, Duke University

Biorganic functionalization of gold thin films and nanocluster mesoscalar assemblies and their resulting optical properties have immense applications ranging from biosensing to nanomedicine. The appealing property is the surface plasmon resonance of those bio-metal ensembles that can be tailored not only by the metal nanoparticles geometry but also by the nature of the biomolecules and the chemistry of the interface. This characteristic is being exploited for realizing nanoscale optical chemosensors and biosensors based on localized surface plasmon resonance of metal nanoparticles.

In this contribution we present and discuss bio- and chemo-functionalization of a novel system based on plasmonic gallium (Ga) nanoparticles (NPs) self-assembled on a large variety of semiconductor substrates including Si, SiC, GaN and GaAs. The advantages of this system for a plasmonic metal/semiconductor sensing platform are presented and compared to the standard gold (Au) nanoparticles system.

The Ga and Au NPs are directly deposited on semiconductors by evaporation and/or plasma sputtering.

For both systems Ga (NPs)/semiconductor and Au(NPs)/semiconductor we discuss semiconductor surface treatments affecting the interface chemistry and the dynamics of interface phenomena playing a role in tailoring the surface plasmon resonance.

Those systems have also been functionalized by bio-molecules, e.g., antigens and antibodies for biosensing and by porphyrins for gas sensing to nitric oxide (NO).

The peculiarity of our study is the exploitation of Plasmonic spectroscopic ellipsometry (HORIBA UVISEL, Jobin Yvon) for the optical monitoring of the plasmon resonance tuning in real time during the nanoparticles deposition on semiconductor surfaces and for the functionalization of metal nanoparticles by anchoring biomolecules to the semiconductor nanostructures.

For these plasmon-enhanced semiconductor nanoscale sensors, the degree of coverage by the porphyrin and/or protein, the aggregation, the type of binding and orientation of biomolecules on a semiconductor nanostructures surface is important for the sensing activity. Therefore, plasmonic ellipsometry is used to investigate the interplay among the nanostructures size and shape, the functionalizing solution concentration and dipping time, the mechanism of anchoring of the functionalizing molecules.

Data are corroborated by atomic force and electrical force microscopies.

This work is supported by the 7FP European Project NanoCharM_Multifunctional NanoMaterial Characterization exploiting ellipsometry and polarimetry

8:40am **BI+NS-MoM2 Geometry and Interactions: How Shape and Intermolecular Interactions Direct the Self-Assembly of Cage Molecules on Au{111}**, ***J.N. Hohman****, M. Kim, P. Zhang, E.I. Morin,* The Pennsylvania State University*, V.E. Balema,* The Sigma Aldrich Corporation*, P.S. Weiss*, The Pennsylvania State University

The self-assembly of cage molecules on metal surfaces enables the manipulation of interface chemistry while eliminating an entire class of defect modes commonly associated with straight-chain molecules such as the n-alkanethiols. The adamantanethiols and carboranethiols have similar geometries and unit cells on Au{111}, but exhibit striking differences in their behavior. We attribute these differences to their contrasting electronic structures and consequent intermolecular interactions. We have characterized the SAMs of positional isomers of several carboranethiols and adamantanethiols by scanning tunneling microscopy, cyclic voltammetry, grazing-incidence Fourier transform infrared spectroscopy, Kelvin probe microscopy, and contact-angle goniometry. We discuss how geometry and intermolecular interactions play competing roles in determining monolayer assembly and stability.

9:00am **BI+NS-MoM3 On the Role of Supramolecular Nanostructure in determining Interfacial Energy and Biological Interactions**, ***F. Stellacci***, Massachusetts Institute of Technology **INVITED**

It is know that specific molecules can spontaneously arrange on various surfaces forming two-dimensional poly-crystalline mono-molecular layers called self-assembled monolayers (SAMs). These organic coatings are used to impart targeted optical, electronic and biological properties to surfaces. Very often SAMs composed of more than one type of molecule (mixed-SAMs) are used to simultaneously impart multiple properties. Scanning tunneling microscopy (STM) studies have shown that, in mixed SAMs, molecules phase-separate in domains of random shape and size.

We will show that when mixed SAMs are formed on surfaces with a radius of curvature smaller than 20 nm they spontaneously phase-separate in highly ordered phases of unprecedented size. The reason for this supramolecular phenomenon is purely topological and can be rationalized through the “hairy ball theorem”. In the specific case of mixed SAMs formed on the surface of gold nanoparticles, the molecular ligands separate into 5 Å wide phases of alternating composition that encircle or spiral around the particle metallic core. This new family of nano-structured nano-materials shows new properties solely due to this novel and unique morphology. For example, we will show that the cell uptake of these particles strongly depends on the particle’s composition and the ligand shell morphology.

9:40am **BI+NS-MoM5 Can We Make Alkanethiol SAM's on Surface of Gold Nanorods?**, ***S. Chakraborty****, S. Lee, V. Perez-Luna*, Illinois Institute of Technology

Gold has been a fascinating element that drew the interest of people since early origins of human history. However, it is just over the last two decades that it gained a resurgence of interest, in conjunction with the advent and development of nanotechnology. Gold nanoparticles have a wide variety of bio-applications such as labeling, sensing, and targeted drug delivery. A directed assembly of gold nanoparticles in the form of nanowires or networks is extensively used as nanodevices. Nanoparticles come in a variety of shapes; spheres, rods and cubes being the frequently observed ones. Surface functionalization facilitates tailoring of the gold surface for various applications. The objective here is to investigate the surface modification of gold nanorods by chemisorption of alkanethiols.

An important property of gold nanorods is their *aspect ratio,* which is defined as the width-height ratio. The lateral surface and edge surface mostly comprise of [100[and [111[surfaces respectively. By appropriate choice of capping agents, the anisotropic surfaces can be tailored for different applications. One of the most-successful methods for synthesis of gold nanorods relies on the use of cationic surfactant CetylTrimethyl Ammonium Bromide (CTAB). CTAB provides stability, size and shape control. The displacement of CTAB allows fuctionalization with other molecules. In this work, the displacement of CTAB is carried out with alkanethiols of varying chain length, viz. 16-mercaptohexadecanoic acid, 11- mercaptoundecanoic acid, 3-mercapto propionic acid. An indirect investigation method is used to analyze the behavior of gold nanorods. Planar surfaces with the same crystalline structures as gold nanorods (111 and 110) are selected for the experiment. Surface modification of planar surfaces is conducted in two steps: formation of CTAB bilayers by immersing planar substrates followed by displacement of CTAB bilayers with alkanethiols.

The experimental studies are characterized by contact angle measurements, fourier transform infrared spectroscopy and cyclic voltammetry. The displacement of CTAB is confirmed by decrease in the contact angle upon formation of carboxyl terminated surfaces and concomitant appearance of stretching band of carboxyl groups. Cyclic voltammetry studies are carried out to calculate the free energy of adsorption of the alkanethiol layers on gold surfaces. Results indicate that longer chain alkanethiols perform better in terms of displacing the CTAB layer from the gold surfaces. The displacement of CTAB is possible on both the lateral and edge surfaces.

10:00am **BI+NS-MoM6 Size-selective Placement of Nanoparticles on a Single Particle Level**, ***P. Bhadrachalam****, S.J. Koh*, University of Texas at Arlington

We present a new nanoparticle placement technique in which single nanoparticles of different sizes recognize different target positions on a substrate and exactly one nanoparticle of specific size is placed on each target position in a self-limiting way. We demonstrate this by using ~50nm and ~20nm colloidal Au nanoparticles (AuNPs) as a model system, where the ~50nm particles are first electrostatically guided onto targeted substrate locations and then the ~20nm particles to different target locations on the same substrate. The electrostatic guiding structure was defined using CMOS-compatible fabrication processes and subsequent functionalization of surfaces using self-assembled monolayers (SAMs) of organic molecules. Using appropriate guiding structure, we present >90% success rate of

~50nm AuNPs placement onto substrate locations targeted for ~50nm AuNPs only. Theoretical calculations for ~20nm AuNPs, which was carried out by solving the non-linear Poisson-Boltzmann equation, revealed that the self-limiting single-particle placement is due to an increase of the free energy barrier after the placement of one nanoparticle onto a targeted substrate location, which prevents the approach of other nanoparticles to the already occupied position. The size-selective placement of single nanoparticles can be explained by dependence of the free energy barrier changes upon the sizes of nanoparticles and guiding structures. The same approach may also be useful for size-selective and single-entity-level placement of other nanoscale building blocks such as nanowires, proteins, and DNA.(Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), and THECB (003656-0014-2006))

Graphene Topical Conference
Room: C3 - Session GR-MoM

Graphene and 2D Carbon Nanostructures
Moderator: M.Y. Zhu, College of William and Mary

8:20am **GR-MoM1 Graphene-based Materials***, **R.S. Ruoff***, The University of Texas at Austin **INVITED**

Our top-down approaches [1] inspired physicists to study individual layers of graphite obtained by micromechanical exfoliation, but our current approaches include growth on metal substrates and judicious use of isotopic labeling (^{13}C vs ^{12}C) to study the kinetics and mechanisms of deposition of large-area graphene and few layer graphene on metal substrates.[3] This talk will focus on our suggested path for obtaining large area growth of high quality graphene in ways compatible with methods of the semiconductor industry. In addition, I will present highlights of published work on polymer matrix composites with graphene as filler[4], on ultracapacitors based on graphene[5], on paper-like materials based on graphene[6], on the use of ^{13}C-labeled graphite (and ^{12}C-pure graphite and graphene) in a variety of areas[7], and on use of graphene as transparent but electrically conductive thin films[7]. *Support of our work by SWAN-NRI, DARPA-CERA, DARPA-iMINT, and prior support by NASA, is appreciated.*

(See also papers on http://bucky-central.me.utexas.edu/publications.htm)

1. Lu XK, Yu MF, Huang H, and Ruoff RS, *Tailoring graphite with the goal of achieving single sheets,* Nanotechnology, **10**, 269-272 (1999).

3. Xuesong Li, Weiwei Cai, Jinho An, Seyoung Kim, Junghyo Nah, Dongxing Yang, Richard Piner, Aruna Velamakanni, Inhwa Jung, Emanuel Tutuc, Sanjay K. Banerjee, Luigi Colombo, Rodney S. Ruoff, *Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils*, published online in *Science* on Science Express (May 7, 2009), hardcopy to appear in *Science*.

4. Sasha Stankovich, Dmitriy A. Dikin, Geoffrey H. B. Dommett, Kevin M. Kohlhaas, Eric J. Zimney, Eric A. Stach, Richard D. Piner, SonBinh T. Nguyen and Rodney S. Ruoff, *Graphene-based composite materials*, Nature 442 (2006) 282-285.

5. Meryl D. Stoller; Sungjin Park; Yanwu Zhu; Jinho An; Rodney S. Ruoff. Nano Letters (2008), 8 (10), 3498-3502.

6. Dmitriy, A. Dikin, Sasha Stankovich, Eric J. Zimney, Richard D. Piner, Geoffrey H. B. Dommett, Guennadi Evmenenko, SonBinh T. Nguyen, Rodney S. Ruoff. Nature, 448, (2007), 457-460.

7. Cai, Weiwei; Piner, Richard D.; Stadermann, Frank J.; Park, Sungjin; Shaibat, Medhat A.; Ishii, Yoshitaka; Yang, Dongxing; Velamakanni, Aruna; An, Sung Jin; Stoller, Meryl; An, Jinho; Chen, Dongmin; Ruoff, Rodney S., Science (2008), 321(5897), 1815-1817.

8. Supinda Watcharotone, Dimitry A. Dikin, Sasha Stankovich, Richard Piner, Inhwa Jung, Geoffrey H. B. Dommett, Guennadi Evmenenko, Shang-En Wu, Shu-Fang Chen, Chuan-Pu Liu, SonBinh T. Nguyen, Rodney S. Ruoff. Nano Letters, 7(7), (2007), 1888-1892.

9:00am **GR-MoM3 Investigation of Process Dependence of Graphene Growth on Nickel Thin Film***, **J. Mun***, KAIST, Republic of Korea*, C. Hwang,* Korea Research Institute of Standards and Science, Republic of Korea*, S. Lim,* National Nano Fab Center, Republic of Korea*, B.J. Cho*, KAIST, Republic of Korea

Recent study on graphene synthesis on metal thin film by chemical vapor deposition in a hydrocarbon ambient has shown promising results for the feasibility of formation of graphene layer over a large area.[1-4] However the graphene layer grown on metal thin film shows various kinds of defects on its surface such as islands of thick graphene layers, carbon dumps, and wrinkles from the different thermal expansion coefficient between metal and carbon, and so on.[2-3] Control of such defects is critical for the technique to be useful, but the mechanism of the defect formation has not been well studied so far. In this work, the effect of various process conditions which affect the quality of graphene on nickel thin film is carefully investigated, including nickel thin film deposition process, ramping up ambient, annealing ambient, annealing temperature, thickness of nickel thin film, etc. During the high temperature annealing process, nickel thin film becomes highly agglomerated and thereby the surface becomes quite rough. Since the segregated carbon amount at nickel grain boundary is different from that segregated from crystalline nickel inside the grain, the agglomeration of nickel directly affects the thickness uniformity of graphene and roughness of graphene surface. It is found that the deposition process of nickel thin film affects the agglomeration and the e-beam evaporation of nickel has shown less agglomeration upon annealing, compared to physical sputtering. It is also found that the annealing temperature in CH_4 is a critical factor to control the amount of thick graphite island on graphene. Furthermore, it is found that the gas ambient during ramping up affects the deformation of nickel thin film. All such detailed process conditions on graphene formation on nickel thin film are carefully investigated and will be presented.

[1] Q. Yu et al., Appl. Phys. Lett. 93, 113103 (2008).

[2] A. Reina et al., Nano Lett. 9, 31 (2009)

[3] K. S. Kim et al., Nature 457, 706 (2009)

[4] L. G. D. Arco et al., IEEE Trans. Nanotech. 8, 135 (2009)

9:20am **GR-MoM4 Evolution of Electrical, Chemical, and Structural Properties of Transparent and Conducting Chemically Derived Graphene Thin Films***, **C. Mattevi***, G. Eda,* Rutgers University*, S. Agnoli,* University of Padova, Italy*, S. Miller,* Rutgers University*, A. Mkhoyan,* University of Minnesota*, O. Celik, D. Mastrogiovanni,* Rutgers University*, G. Granozzi,* University of Padova, Italy*, E. Garfunkel, M. Chhowalla*, Rutgers University

An alternative path to graphene is represented by graphene oxide (GO) that can be readily exfoliated and then deposited from suspension on variety of substrates. GO is an insulator but controlled reduction provides tunability of the electronic properties leading the possibility of accessing zero-band gap graphene. However, the GO structure and opto-electronic properties at different stages of reduction are largely unknown. Here we focus on a detailed description of opto-electronic properties, chemical state [1] and structure [2] of single and few-layered GO at different stages of reduction. The residual oxygen forms sp3bonds with carbon atoms in the basal plane such that the carbon-carbon sp2 bonding fraction in fully reduced GO is ~ 0.80. The oxygen disrupts the transport of carriers delocalized in the sp2 network, limiting the mobility and conductivity of reduced GO thin films. Our analysis reveals that removal of oxygen to achieve sp2 carbon fraction of > 0.95 in GO should lead to properties that are comparable to graphene.

[1] C. Mattevi et al.“Evolution of electrical, chemical, and structural properties of transparent and conducting chemically derived graphene thin films” Adv. Funct. Mater. *In press*.

[2] K. A. Mkhoyan et al.” Atomic and electronic structure of graphene oxide” Nano Lett. vol.9, (2009), p 1058.

9:40am **GR-MoM5 Plasma-based Approach to Controlling the Oxygen Concentration in Graphene Oxide***, **S.G. Walton***, M. Baraket, E.H. Lock*, Naval Research Laboratory

Graphene and graphene oxide have attracted widespread interest because of their unique structural and electronic properties, which lend themselves well to the production of nanoscale electronic and sensing devices. Indeed, graphene is a single monolayer thick carbon sheet with remarkably high electron mobility. The addition of oxygen increases the sheet thickness and decreases this mobility and, more interestingly, determines both the conducting and reactive properties of the material. One significant impediment to realizing the potential of graphene oxide is the development of an industrially viable approach to producing large area substrates of well-controlled oxygen concentration. In this respect, plasmas are an ideal candidate but problems associated with the large fluxes of energetic ions are a significant concern. The Naval Research Laboratory has developed a plasma processing system that is characterized by a uniquely low incident ion energy, in the range of a few eV, at or near the carbon-carbon and carbon-oxygen bond strength. We discuss the use of this system to reduce the oxygen concentration of graphene oxide. We examine the plasma processing conditions, plasma characteristics, and the resulting properties of the material in an effort to understand reduction mechanisms. This work was supported by the Office of Naval Research.

10:00am **GR-MoM6 Graphene Growth on Transition-Metal Thin Films**, ***P.M. Albrecht***, *E.A. Sutter, P.W. Sutter*, Brookhaven National Laboratory

Epitaxy on transition metal substrates is a promising approach for the large-scale synthesis of graphene for potential applications in microelectronics and sensing. In particular, the controlled layer-by-layer growth of graphene on Ru(0001) has been shown to result in macroscopic monocrystalline graphene domains with lateral sizes greater than 200 microns, perfect thickness uniformity, and very low defect density [1]. Whereas the first graphene layer interacts strongly with the Ru(0001) template, the second layer is essentially decoupled from the metallic support, thus preserving the atomic structure and exotic electronic properties of isolated single-layer graphene [2]. A viable route towards large-area, free-standing graphene would be to grow on polycrystalline transition-metal thin films rather than single crystals, followed by the dissolution of the metal template to detach the graphene and transfer it to another support. Two groups have recently demonstrated the growth of few-layer graphene on polycrystalline Ni films using this method [3, 4].

Here, we report a study of graphene growth on Ru thin films. The polycrystalline Ru template layers were deposited on SiO$_2$ by magnetron sputtering in ultrahigh vacuum. We used in-situ annealing and scanning tunneling microscopy (STM) to study the recrystallization and grain growth of the Ru template, crucial to forming a starting surface suitable for the growth of macroscopic graphene domains. STM also provided a detailed understanding of the interaction of the growing graphene layer with Ru grains with different surface orientations, grain boundaries, as well as highly vicinal surfaces. Cross-sectional transmission electron microscopy (TEM) was used to directly image the graphene-metal interface for the first time. Our results provide a basis for the scalable synthesis of graphene on transition metal thin films.

[1] P. W. Sutter, J.-I. Flege, and E. A. Sutter, Nature Mater. 7, 406 (2008).

[2] E. Sutter, D. P. Acharya, J. T. Sadowski, and P. Sutter, Appl. Phys. Lett. 94, 133101 (2009).

[3] A. Reina et al., Nano Lett. 9, 30 (2009).

[4] K. S. Kim et al., Nature 457, 706 (2009).

10:40am **GR-MoM8 Is Fullerene-Intercalation in Graphite a Vehicle to Graphene Surface Layer Doping?**, ***P. Reinke***, *S. O'Donnell*, University of Virginia

In order to exploit the extraordinary properties of graphene several materials-based challenges have to be addressed to reach full device functionality. The challenges include opening and control of a bandgap, n- and p type doping while preserving the ambipolarity at the K-point, and sustaining the high mobility of charge carriers. We introduce here a novel and highly versatile method for the modulation of the electronic properties of graphene, which is based on fullerene (C$_{60}$)-graphite intercalation compounds (C$_{60}$-GIC). The goal is to electronically decouple the top graphene sheet from its substrate through the introduction of an intercalated layer of fullerene molecules, which are a wide bandgap material and thus do not significantly perturb the bandstructure around the Dirac point of graphene. The fullerene layer can subsequently be doped and thus the charge transfer to the graphene is controlled via the modulation of the intercalated fullerene layer. The synthesis of the C$_{60}$-GICs is achieved by an annealing process, where the supersaturation of the gasphase with fullerenes is used to drive the molecule into the graphite lattice. The parameter space for successful intercalation is controlled by the substrate temperature, fullerene concentration and the defect structure of the graphite. The intercalation process is observed with scanning tunneling microscopy and spectroscopy which is probes the geometric and electronic structure of the top layer. The presence of sub-surface fullerenes is detected through the appearance of a Moire pattern and a weak distortion of the topography, usually presented in a well-defined area around step edges. The spatial distribution of intercalated regions is used to describe the kinetics of the intercalation process and to elucidate the mechanistic aspects of the material synthesis. The graphene doping through the incorporation of a second dopant (e.g. K) in the C$_{60}$ layer is investigated with STM. The electronic structure of the top graphene layer is measured with STS, and the spatial distribution of charge-puddles and their relation to the sub-surface C$_{60}$ lattice will be discussed.

11:00am **GR-MoM9 1 nm Thin Carbon Nanosheets: Two-Dimensional Functional Materials**, ***A. Gölzhäuser***, University of Bielefeld, Germany **INVITED**

A route for the fabrication of 1 nm thin and free-standing carbon films and membranes, whose electrical and mechanical behavior as well as surface functionalization can be tuned, is presented. Self-assembled monolayers (SAMs) of aromatic biphenyls are cross-linked by electron irradiation and then detached from the surface. This results in mechanically stable carbon nanosheets with the thickness of a single molecule and sizes up to several cm^2. Upon annealing at ~1000K, the cross-linked monolayers transform into a graphitic phase that consists of nanosize patches of graphene [1]. This transition is accompanied by a drop of the sheet resistivity from ~10^8 to ~10^2 kΩ/sq and mechanical stiffening from ~10 to 50 GPa. Hence, nanosheets represent two-dimensional materials with tunable conductivity and stiffness. When transferred onto SiO$_2$/Si substrates, nanosheets can be visualized by Raleigh interference contrast. By using SAMs of appropriate biphenyls, a chemical surface functionalization of the nanosheets can be achieved, which allows their tailoring for technical applications. Nanosheet devices are presented and applications in microscopy as well as in polymer- and biophysics are discussed.

[1] A. Turchanin, A. Beyer, Ch. T. Nottbohm, X. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Gölzhäuser, *Adv. Mater.* **21,** 1233 (2009)

11:40am **GR-MoM11 Catalytic Property and Morphology of Pt Clusters on Graphite Surface**, ***J. Nakamura***, *T. Kondo, K. Watahiki, Y. Iwasaki, J. Oh, T. Suzuki, Y. Honma, D. Hatake*, University of Tsukuba, Japan

Understanding the interface interaction between platinum nano-cluster and carbon supports composed of graphitic materials is one of the most important need in development of electrocatalysts for fuel cell. We have studied the effects of the interface interaction on the catalytic properties using model catalysts of Pt-deposited highly oriented pyrolytic graphite (HOPG) by IETS-STS-STM, TPD, and molecular/atomic beam technique. The deposited Pt clusters show unique morphology and catalytic properties. That is, the shape of Pt clusters (1-5 nm) is a raft-like structure with one or few atomic heights. The Pt clusters show quite high catalytic activity for H$_2$-D$_2$ exchange reaction at 24 Torr. Desorption peak of CO from the Pt was observed at a low temperature of 300 K. The significant modification is ascribed to the interface interaction between Pt atoms and graphite surface. In the STM observation, it was found that Pt atoms are located on beta-carbon, indicating the shrinkage of Pt-Pt distance about 13% compared to that of the bulk Pt. The modification in the catalytic properties and the electronic structure of the flat Pt clusters is thus ascribed to the reduction in the lattice constant of Pt. It is explained that the d-band center of Pt shifts away from the Fermi level due to the reduction in the lattice constant. We show evidence of the interface interaction between Pt and graphite here. Distinct electronic states of the graphite near the Fermi level, "non-bonding π electronic states", were observed at the carbon atoms in the vicinity of the Pt clusters by STS measurements, which is interpreted by our newly proposed model: the conjugated bond of graphite between alpha- and beta-carbon atoms are re-hybridized into two p$_z$-orbitals, where the p$_z$-orbital of beta-carbon would be hybridized with a d-orbital of the Pt atom and the other p$_z$-orbital of alpha-carbon becomes a non-bonding p-orbital. Consequently non-bonding p electronic states forms at the alpha-carbon atoms of graphite in the vicinity of the Pt cluster. The proposed model is consistent with our experimental result of scanning tunneling microscopy and inelastic electron tunneling spectroscopy (IETS) measurements as well as STS results and our first-principles density functional calculations of the graphene sheet with a Pt cluster.

History Session: Centennials of Wireless Broadcasting
Room: B2 - Session HI-MoM

History Session: Centennials of Wireless Broadcasting
Moderator: R.K. Waits, Consultant

8:20am **HI-MoM1 Marconi and the First "Vacuum Tube": More than 100 years of Nothing at Work**, ***B. Lee***, San Francisco Attorney **INVITED**

The history of the discovery of the uses of nothing, i.e., vacuum, pleases the mind. In communications, Guglielmo Marconi utilized a vacuum device about 1898. The "coherer" detected radio frequency energy rendering it sensible to people through other devices. Marconi evacuated this device to improve its performance. In doing so, he illustrated a deeper principle: eliminate the equivalent of "friction" and see (and enjoy and exploit) the true operation of nature. Newton's celestial mechanics also illustrate this principle, which has an analogy in economics as well.

Other communications pioneers also used vacuum devices to detect the signals of the then new wireless telegraphy. Notably, Marconi, through the work of John Ambrose Fleming, implemented the vacuum diode, the "Fleming Valve," thereby advancing the art. Lee deForest put the famous "grid" between the filament cathode and anode of the Fleming vacuum diode, and created the primary technology of 20th century communications, the triode vacuum tube as an amplifier and oscillator.

When Fleming heard about that innovation, he is reported to have said: "I wish I'd thought of that!" Marconi, being the businessman he was, implemented these new vacuum devices as quickly as he could, as did all the other wireless pioneers. ##

9:00am **HI-MoM3 Charles Herrold, Inventor of Radio Broadcasting**, ***M.H. Adams***, San Jose State University **INVITED**

The Charles Herrold story was almost lost in history. It began in 1958 with San Jose State University Professor Gordon Greb's class project to identify and honor a pioneer in broadcasting. Professor Greb accidentally uncovered the Herrold information at a local museum, research was done, and an event introducing the story was sponsored by the university and KCBS, the direct descendant of Herrold's original 1909 work. Greb then wrote a 1959 journal article, "The Golden Anniversary of Broadcasting" in the *Journal of Broadcasting,* based on collected family papers, oral histories/interviews of eyewitnesses, and other evidence.

It was the first time a national academic audience heard about Charles Herrold. Most just assumed that broadcasting began in 1920 with KDKA. San Jose State University Professor Mike Adams joined Greb in 1988 to revive the Herrold story. Adams believed that the Herrold evidence, while based on eyewitnesses and original family documents, remained a local story, not taken seriously by anyone beyond the Bay Area. A PBS documentary, "Broadcasting's Forgotten Father: The Charles Herrold Story" resulted. Adams and Greb also knew that the only way for the Herrold story to gain national credibility was for a well-researched, scholarly book to be published. The authors made trips East, to the Clark papers at the Smithsonian Institution, the New York Public library, and the Antique Wireless Association archives in Rochester NY. Their goal was to find other examples of pre-1920 broadcasting similar to that carried out by Herrold in San Jose. The two found several important primary research documents showing Herrold broadcasting pre-1910, further evidence not in the original Herrold papers. Several major articles and the book, *Charles Herrold, Inventor of Radio Broadcasting* (Mcfarland Press 2003), resulted. The book presents the evidence of Herrold's first broadcasting station, and puts it into the context of other pre-1920 radiotelephone inventors.

Today, there is no real agreement as to a single "first station." Most historians agree that KDKA gets credit for the first "commercial" license in 1920, de Forest for his 1916 broadcast of the Hughes-Wilson presidential election, and Herrold for broadcasting entertainment on a regularly-scheduled basis, pre-announced, to an audience, 1909-17. What is known and stated in the Herrold book is that the authors found first person, written evidence indicating that Herrold beginning in 1909 was the first to intentionally broadcast entertainment programming to a known audience.

9:40am **HI-MoM5 Mutual Evolution of Vacuum and Broadcasting Technology**, ***S. Rutherford***, Duniway Stockroom Corp. **INVITED**

Since the earliest days of radio tubes/valves, there has been a mutually beneficial evolution of radio and vacuum technologies. Whether broadcasting or transmission, receiving or amplification types of tubes; whether vacuum tubes or semiconductor circuits - vacuum production, processing, measurement and maintenance have all profited from the evolution of radio technology. The 'discovery' of vacuum involved observations of the operation of a mercury barometer. Early vacuum pumps refined the mercury-piston approach, but then relatively rapid evolution of both compression mechanism and sealant/medium took place. In later years, the introduction of a variety of traps and capture pumps, starting with flash getters and leading to getter-ion pumps, greatly improved the cleanliness of the vacuum tube environment. Pressure measurement likewise evolved from the barometric model to include thermal gauges, based on observations of thermal effects in vacuum tubes; ionization gauges based directly on the triode radio tube; and cold cathode gauges related to magnetron and ion pump technologies This rich history of mutually improving development of vacuum and radio technology has also resulted in enhancing the application of vacuum technology to many other new and expanding applications. In fact, some of these new applications have led to the continuously advancing replacement of vacuum tubes!

Nanometer-scale Science and Technology
Room: L - Session NS+BI-MoM

Nanowires and Nanoparticles I
Moderator: L.E. Ocola, Argonne National Laboratory

8:20am **NS+BI-MoM1 Zirconia Nanoplatelets for use in Dental Restoratives**, ***K. Coulter***, *V.Z. Poenitzsch, S. Wellinghoff, B. Furman, M. Rubal, D. Nicolella, K. Chan*, Southwest Research Institute

Photopolymerizable composites containing very high volume fractions (>50%) of radio-opaque nanoplatelets in a low polymerization shrinkage, liquid crystalline (LC) monomer mixture are being developed as dental restoratives. The LC monomer promotes the organization of the nanoplatelets into either a smectic or columnar, colloidal liquid crystal structure with significantly enhanced strength. Further, theoretical calculations suggest that the tetragonal form of the yttria-stabilized zirconia nanoplatelets that SwRI is producing by a roll-to-roll, e-beam evaporation process can be induced to transform into a less dense monoclinic form in the presence of the hydrostatic tensile stresses expected at a growing crack tip within the composite resin. This transformational volume expansion coupled with the inherent ductility of the surrounding LC polymer matrix results in substantial improvements in dental composite wear resistance. SwRI has successfully coated onto a 200nm pitch, nanoembossed PET film in single run lengths of hundreds of meters, a 10 nm alkali halide release layer to produce a 50nm thick zirconia film of tetragonal crystal form which is subsequently removed by dissolving the alkali halide layer in water. The nanoembossed pattern transfers to the zirconia layer to produce nanoplatelets. three specific problems have been encountered including: (1) producing tetragonal zirconia of consistent morphology in different ca 100 meter runs, (2) complete fracture along the nanoembossed pattern, (3) color in the zirconia, most probably resulting from oxygen depletion and sub-4+ zirconia oxidation states. In this paper we will present the fabrication process and challenges in producing the nanoplatelets and present some of the preliminary composite data.

8:40am **NS+BI-MoM2 Formation of Metallic Nanoclusters on TiO_2 by Deposition and Sputtering**, ***A.B. Arjad***, *J.A. Yarmoff*, University of California, Riverside

The discovery that Au nanoclusters are catalytically active when supported in an oxide matrix[1] has led to an abundance of surface studies, particularly those concentrating on metal nanoclusters deposited on single crystal TiO_2. For example, STM showed that Au clusters grow on TiO_2(110) without a wetting layer and that the size of the clusters increases as more metal is deposited.[2] We previously used low energy alkali ion scattering to interrogate such clusters grown by evaporation, measuring the neutral fraction of the backscattered ions with time-of-flight spectroscopy.[3] We were able to show that the neutralization depends on the electronic structure of the clusters, and therefore changes as a function of cluster size. Our group also demonstrated a novel method for the production of nanoclusters by Ar^+ sputtering a thin Au film deposited on TiO_2.[4] As this initial work was performed with Au, it is not clear whether nanoclusters displaying quantum size effects could be fabricated by sputtering other materials. In the work presented here, Ag and Pt are evaporated onto TiO_2(110) and thin films of these metals are sputtered. The materials are then interrogated via the scattering of 2.5 keV Na^+. It was found that while both Pt and Ag form nanoclusters by evaporation, only Pt forms nanoclusters after sputtering. This may be due to differences in the surface free energy of the metals, or of the propensity of Ag to oxidize. Future efforts will include temperature programmed desorption to test the chemical activity of the metal nanoclusters, as well as the use of other substrates.

[1] M. Haruta, et al., J. Catal. **144**, 175 (1993).

[2] M. Valden, X. Lai and D.W. Goodman, Science **281**, 1647 (1998).

[3] G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **92**, 216801 (2004).

[4] P. Karmakar, G.F. Liu, Z. Sroubek and J.A. Yarmoff, Phys. Rev. Lett. **98**, 215502 (2007).

9:00am **NS+BI-MoM3 Towards Emergence of New Function by Engineering Materials: Colloidal Nanocrystals as Building Blocks for Nanocomposites and Assemblies**, ***M.L. Curri***, CNR IPCF, Italy **INVITED**

Increasing attention has been devoted to the properties of materials in nanophase state, which are highly dependent on their size and shape and can be dramatically different from those of the corresponding bulk phase materials. Such geometry dependent characteristics result essential for design novel functional materials with tailored characteristics, revealing a high impact on fundamental aspects as well as on potential technology applications. Fine tuning of the nanomaterial electronic, optical, magnetic, thermal, mechanical, and chemical properties opens possibilities for their wide applications in several technological fields. In this sense the basic nanosized building blocks of such complex structures play a crucial role and the extent to which nanocrystals (NCs) and nanoparticles (NPs) can be fabricated, engineered and their properties tailored is central. Chemical strategies are now able to provide highly processable NCs, possessing an adjustable interface with the external environment, able to tune their specific chemical reactivity towards the surroundings1. Equally decisive is the scheme used to convey the instruction for assembly and organization into the inorganic NPs. Assembly can be spontaneous (self assembly), guided by the intrinsic information coded into the building blocks, and/or driven by external stimuli, templates, chemical and/or physical forces.1,2 The complexity of the formed structures depend on a variety of factors, ranging from the type of the single structural component, the length scale along which the structured material is achieved, the kind of mechanism ultimately involved for the creation of the final architectures. The NC based structures, either hierarchical organized or nanocomposite in nature, can show original emergent properties which cannot be readily envisioned from the building block original properties, while can be observed to arise in the originated mesostructure of nano-objects.3 The potential to design and fabricate such nanostructured materials with unprecedented functionality open the routes for applications in biomedical, optical, electronic, catalytic and light energy conversion systems.

1. E. Fanizza, P. D. Cozzoli, M. L. Curri, M. Striccoli, E. Sardella, A. Agostiano (2007) Adv.Funct. Mater. 17 201-211.

2. M. L. Curri, R. Comparelli, N. Depalo, E. Fanizza, M. Striccoli “Patterning and Assembling of Inorganic Nanocrystals” in Nanomaterials: Inorganic And Bioinorganic Perspectives Edited by C. M. Lukehart and R. A. Scott, Chichester, UK: John Wiley & Sons, Ltd, pp 327-356,

3. J. Y.Kim, C. Ingrosso, V. Fakhfouri, M. Striccoli, A. Agostiano, M. L. Curri, J. Brugger (2009) Small 5 1051-1057.

9:40am **NS+BI-MoM5 The Direct Writing of Nanoscale Patterns of Nanoparticles and Polymer–Nanoparticle Composites**, ***P. Sheehan***, *W.-K. Lee,* Naval Research Laboratory*, W. King, Z. Dai*, University of Illinois, Urbana-Champaign

In thermal Dip Pen Nanolithography (tDPN), a heatable AFM cantilever regulates the deposition of an ink through controlled melting, much like a nanoscale soldering iron. Control over writing is exceptional—deposition may be turned on or off and the deposition rate easily changed without breaking surface contact. Moreover, the technique may be performed in UHV and is compatible with standard CMOS processing. tDPN has been successful at depositing materials ranging from semiconductors to insulators to metals at speeds up to 200 µm/s.

Recently, we have become interested in directly depositing nanoparticles-polymer composites. Nanoparticles and nanoparticles–polymer composites offer many new capabilities that could greatly advance nanoelectronics, data storage, biosensors, and optical imaging applications. However, these applications often require that the nanoparticles or composites be formed into nanostructures that are precisely deposited on a surface or in a device. This requirement has spurred the development of many new nanolithographies but, to date, they have exhibited relatively low resolution (>~100 nm), a lack of generality to a range of materials, or the requirement of many serial processing steps. With tDPN, we can deposit with nanoscale precision a wide range of polymers (PMMA, P(VDF-TrFE), polyethylene) that contain metallic nanoparticles, semiconducting nanoparticles, or small molecules. An oxygen plasma can remove the polymer to reveal evenly dispersed nanoparticles or, for some combinations, precisely-placed 10 nm wide rows of nanoparticles. The flexibility and precision of this approach should greatly speed the advent of AFM tip based nanomanufacturing.

10:00am **NS+BI-MoM6 Synthesis and Structural Characterization of Fe-O Nanonetworks**, ***G.C. Franco***, *C.V. Ramana*, University of Texas at El Paso

Iron (Fe) oxides and hydroxides have been the subject of numerous investigations for many years. Fe oxides and hydroxides find application in chemical catalysis, magneto-electronics, energy storage and conversion, and nuclear industry. The properties and phenomena of these materials are influenced by the morphology and size. The present work is performed to grow high-quality and ordered structure Fe oxides by simple wet-chemical method at a relatively low temperature. Fe oxides and hydroxides have been prepared in aqueous media by precipitation of iron nitrate and ammonium hydroxide. Their growth and structural characteristics have been investigated using x-ray diffraction (XRD) and high-resolution scanning electron microscopy (HRSEM). The approach is preparing different solutions of Fe particles in suspension and acetic acid at different concentrations and subject to heat treatment at 100 °C. XRD analyses indicate that the solids obtained from aqueous stage exhibit goethite (α-FeO(OH)) with average particle size 2-3 nm, while the samples with acetic acid addition shown hematite (α-Fe_2O_3) with average size ~20 nm. HRSEM images confirm the presence of particles ~100 nm in samples with no acetic acid. HRSEM indicate that the samples with acetic acid exhibit nanoparticles ~20 nm with small spots within the particles. In addition, SEM shows the presence of net-shaped structures and particles with high-dense porosity within the nano-regime depending on the concentration of acetic acid. The experiments also confirm that Fe oxide nano-particles and networks are stable to a temperature of 500 °C. The results obtained on the growth, structure, and properties of the grown Fe-based nanomaterials will be presented and discussed in detail.

10:40am **NS+BI-MoM8 Synthesis of Shape Controlled Sinter Resistant Nanoparticles**, ***N. Shukla***, *M. Nigra*, *A.J. Gellman*, Carnegie Mellon University

We report synthesis of shape controlled, sinter resistant, core shell nanoparticles. The synthesis conditions allow control of the shell shape and the preparation of hexagonal shells and spherical shells. The 3D structures of these particles have been studied using angle resolved high resolution TEM. 2D cross sectional TEM images show that the cores are not positioned at the centers of the shells. By rotating the nanoparticles and monitoring the apparent motions of the cores in the 2D cross sectional images it is possible to determine the radial position of the core with respect to the center of the shell. The distribution of core positions within the core shell structures is bimodal. These observations suggest that the Fe shells grow on the Pt cores by a nucleation process rather than layer-layer growth.

11:00am **NS+BI-MoM9 Fabrication and Characterization of Carbon Nanostructures; Optical, Mechanical and Chemical Properties**, ***H. Fredriksson***, *T. Pakizeh,* Chalmers University of Technology, Sweden*, J. Cardenas,* University of Oslo, Norway*, M. Käll, B.H. Kasemo, D. Chakarov*, Chalmers University of Technology, Sweden

Nanosized carbon particles are present in many different context and applications. Examples include, aerosols and interstellar dust, inks, lubricants, composite materials and electronics. Investigations of the physical properties of such nanocarbons are therefore well motivated. We present a systematic investigation of the optical, mechanical and chemical properties of graphite and amorphous carbon nanostructures with different size. Hole-mask colloidal lithography and oxygen reactive ion etching is used to fabricate supported carbon nanostructures with well-defined diameters ranging from ~100 to 350 nm and heights from ~50 to 200 nm. Optical absorption/extinction spectra of these samples, as well as finite difference time domain (FDTD) calculations, reveal resonant absorption of visible light, both for the graphitic and for the amorphous carbon structures. The spectral maxima of the absorption peaks are correlated to the nanostructure diameters and heights. These optically resonant nanostructures are then further investigated using Raman spectroscopy, and compared with measurements from macroscopic graphite crystals. We show that the limited size has little influence on the mechanical properties of the graphite, i.e. the nanostructures have the mechanical properties of crystalline graphite. However, a slight enhancement of the Raman scattering intensity, correlated to the resonant absorption in the nanostructures is observed. Upon increasing the laser power we also observe distinct peak-splits and -shifts as well as increasing anti-Stokes signal intensity, suggesting selective heating of the nanostructures. Furthermore, the correlation between size and optical absorption have been used to follow the oxidation-driven size decrease of amorphous carbon nanostructures, relevant as model systems for investigations of soot oxidation. It is shown that the peak characteristics (spectral position and amplitude) are very sensitive signatures of the nanostructure size and that this can be used to accurately measure very low oxidation rates, using simple optical absorption techniques.

11:20am **NS+BI-MoM10 Microscopic and Spectroscopic Studies of Photoactive Supermolecular Porphyrin Assemblies**, ***U.M. Mazur***, *K.W. Hipps, B.C. Wiggins, B.A. Friesen*, Washington State University

Synthetic porphyrins form excitonically coupled ring- and rod-shaped nanostructures, which are of interest for their potential applications in optoelectronic devices and solar cells. Nanorods produced from the sodium salt of tetrakis(4-sulfonatophenyl) porphyrin, TSPP, dissolved in acidic aqueous solutions, were deposited onto Au(111) substrates and were imaged by scanning probe microscopy. Ambient and UHV scanning tunneling microcopy, STM, images revealed individual rods with diameters of 25-40 nm and lengths of hundreds of nanometers. High resolution STM images of TSPP on Au(111) showed that the rods are composed of disk-like building blocks approximately 6.0 nm in diameter. We speculate that the disks are formed by a circular *J*-aggregation of 14-16 overlapping electronically coupled porphyrin chromophores and that this circular porphyrin organization is driven by nonplanar distortions of the porphyrin diacid. X-ray photoelectron spectroscopy, XPS, was employed to investigate the structural changes in TSPP associated with the protonation of the porphyrin ring and aggregation. Scanning tunneling spectroscopy, STS, results indicate high conductivity of TSPP nanorods that can be attributed LUMO based conductivity in the nanorods.

Our results shed light not only on the structural model for TSPP basic aggregate unit but also on the conduction mechanism within the TSPP nanorod structure.

11:40am **NS+BI-MoM11 Solid-State Tunneling Spectroscopy of Individual Nanoparticles**, ***R. Subramanian***, *P. Bhadrachalam, V. Ray, S.J. Koh*, University of Texas at Arlington

Semiconducting nanoparticles are increasingly finding innovative applications in many areas of science and technology such as bio-medicine, solar-energy harvesting, and photonics. For effective use of nanoparticles for these applications, it is necessary to know their electronic structures and efficient and accurate techniques to measure them are desired. We present a new technique to directly probe the energy levels of individual semiconducting nanoparticles in which the units to measure the electronic structures are fabricated using CMOS-compatible processes. This technique not only enables us to probe energy levels of an individual nanoparticle, but allows carrying out many such measurements from numerous units fabricated with a single-batch parallel processing. The energy levels were directly obtained with the I-V measurement through double barrier tunnel junctions that were formed when the nanoparticles were placed between vertically separated source and drain electrodes. The band gap (E_g~1.92eV) and energy level spacings (ΔE ~ 130meV, $\Delta E_{p\text{-}d}$~ 96meV and $\Delta E_{d\text{-}f}$~ 103meV) were measured directly from the current-voltage and differential conductance spectra for colloidal CdSe nanoparticles (~7nm). Measurements for core-shell semiconducting nanoparticles (such as InP/ZnS) will also be presented. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), and THECB ARP (003656-0014-2006))

Plasma Science and Technology
Room: A1 - Session PS1-MoM

Advanced Interconnect Etch
Moderator: M. Armacost, Applied Materials, Inc.

8:20am **PS1-MoM1 Modification Mechanisms of Porous Low-k SiOCH Film during Plasma Ashing Processes**, ***K. Kurihara***, *T. Imamura, K. Yamamoto, H. Hayashi, Y. Nakasaki*, Toshiba Corp., Japan **INVITED**

Porous low-k SiOCH materials are being introduced in order to realize highly reliable interconnects for sub 32 nm node LSI. There are still several problems regarding its use. One of the problems is the damage to low-k materials during etching and ashing processes. During resist ashing process the loss of hydrophobic groups in the pore leads to the uptake of water into the film and results in an increase in k value. To overcome this issue, two approaches are considered. In one approach, the low-k material itself becomes resistant to the plasma processes. In the other, the low-damage plasma processes are developed. The collaboration of both approaches is probably necessary to achieve interconnection for future device generations. We studied the above two issues from the viewpoint of fundamental mechanisms. Concerning the former issue, we have examined the dependence of the plasma resistance of SiOCH films on the film structure, which contained the methylene-bridge ($Si\text{-}CH_2\text{-}Si$) and/or the methyl groups. It was found that the decrease in the amount of carbon in the SiOCH film containing only methyl groups is larger than that in the film containing methylene bridges. Concerning the latter issue, we have investigated the mechanism of ashing process using CO_2 plasma. It was found that a densified layer was formed at the outermost surface of the SiOCH film during ashing, and the layer plays an important role in the control of water absorption into the film. This ashing process resulted in lower damage to the SiOCH film compared with O_2 or N_2/H_2 plasmas.

9:00am **PS1-MoM3 Oxygen Plasma and Radical Interactions with Ultralow-K Organosilicates; Fundamental Damage Mechanisms**, ***J. Kelber***, *S. Behera, S. Manandhar, S. Gaddam*, University of North Texas

Exposure of ultralow-k organosilicate ("SiCOH") materials to oxygen plasma induces methyl group abstraction and other changes leading to significant increases in k value. We present ex situ FTIR and in situ XPS data for O_2 plasma and thermal ($E_{kinetic}$ < ~ 0.1 eV) electronic ground state atomic O (thermal $O(^3P)$) interactions with SiCOH films. The data yield new insight concerning the fundamental mechanisms and kinetics of oxygen plasma-induced CH_3 abstraction, and how these are affected by organosilicate pore structure. FTIR measurements indicate that methyl group abstraction kinetics in the presence of a direct O_2 plasma are diffusion-dominated, and that this diffusion is directly related to SiCOH diffusivity (pore interconnectedness) rather than total pore volume. Pre-treatment of a high porosity/high diffusivity material with He plasma prior to O_2 plasma exposure sharply limits CH_3 abstraction in a manner similar to that exhibited by a vicinal high porosity/low diffusivity material—evidence that He pretreatment results in closure of pore channels. Exposure to $O(^3P)$ from a thermal source (1300 K) results in changes in FTIR spectra similar to exposure to O_2 plasma, indicating that thermal $O(^3P)$ is a major reactant in the diffusion-dominated CH_3 abstraction mechanism. In situ XPS analysis of thermal $O(^3P)$/organosilicate interactions indicate that carbon loss and O/OH incorporation in the organosilicate surface region occur *concurrently*; i.e., Si-C bond scission and Si-O formation are related processes resulting from interaction with $O(^3P)$. This conclusion is supported by recent ab initio DFT-based molecular simulation (AIMDS) results recently reported by Jincheng Du and co-workers (Chaudhari, et al., submitted) that also indicate energy barriers to O/SiCOH interactions are extremely trajectory-sensitive, thus providing a rationale for the experimentally indicated O diffusion mechanism. The experimental and theoretical data also provide insight concerning O interactions with other Si/C based materials, such as SiC, and the implications of this work for processing of SiC will be discussed.

Acknowledgments: This work was supported by the Semiconductor Research Corporation under task ID 1862.001 and by the Robert Welch Foundation under grant B-1356. The authors thank Dr. G. A. Antonelli for providing samples and for useful discussions.

9:20am **PS1-MoM4 Synergistic Damage Effects of Vacuum Ultraviolet Photons and O_2 in SiCOH Ultra-Low-*k* Dielectric Films**, ***J. Lee***, *D.B. Graves*, University of California-Berkeley

Damage originating from plasma processing is a persistent problem with porous ultra-low-*k* dielectric films, such as SiCOH. Although most of the proposed mechanisms of plasma-induced damage focus on the role of ion bombardment and radical attack, vacuum ultraviolet (VUV) photons have been shown to play a role in bond modification of this material [1]. Using a vacuum beam apparatus with a calibrated VUV lamp, we show that 147 nm VUV photons cause bond scissioning in SiCOH, resulting in subsequent, post-exposure adsorption and reaction of water vapor from the atmosphere. Furthermore, the level of damage increases significantly under simultaneous exposure to VUV photons and O2. The role of photodissociation (and O radical formation) is shown to be negligible for the experimental conditions. The vacuum beam photon exposures are representative of typical plasma processes. Fourier-transform infrared (FTIR) spectroscopy implies that O2 itself reacts with photo-generated Si radical sites, replacing scissioned Si-C bonds with Si-O bonds (and ultimately SiOH groups) and making the surface more hydrophilic than with photon exposure alone. The present results demonstrate that VUV photo-generated surface reactions can be potent contributors to ultra-low k dielectric SiCOH film plasma-induced damage, and suggest that they could play analogous roles in many other plasma-surface interactions.

[1] Jinnai, B. et al., Damage Mechanism in low-dielectric (low-*k*) films during plasma processes. *Journal of Vacuum Science & Technology B*, 2008, 26(6): p. 1926.

9:40am **PS1-MoM5 Sidewall Modification of Porous SiOCH Ultra Low k Materials Induced by Reducing and Oxidizing Post Etching Plasma Treatments**, ***R. Bouyssou***, *T. Chevolleau,* CNRS-LTM, FRANCE*, N. Posseme, T. David, Ch. Licitra,* CEA-LETI-MINATEC, France*, A. Ostrowsky, C. Verove,* STMicroelectronics, France*, O. Joubert*, CNRS-LTM, France

From 32 nm interconnect technology node and below, porous SiOCH (p-SiOCH) materials presenting a porosity higher than 25% and a dielectric constant lower than to 2.5 are introduced. However the porosity introduction leads to complex integration issues. One of them is the high sensitivity of porous materials to radical species generated by the plasma during etching and ashing processes. An other serious issue brought by the porosity is the possibility of metal diffusion into the dielectric during conformal metallic barrier deposition. In order to surmount those issues, the optimization of post etching plasma treatments (PET) using reducing and oxidizing chemistries present some interest since such treatments can be efficient not only as post-etching cleaning processes of the sidewall patterns and reactor walls but also potentially as "pore sealing-like" processes to prevent metal barrier diffusion.

In this work, plasma induced modifications of p-SiOCH sidewalls have been investigated using volume and surface analyses techniques such as ellipsometric porosimetry (EP), infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS) and HF decoration techniques (resin encapsulation followed by a HF dip). After p-SiOCH patterning (porosity of 27% and k=2.35) using a TiN hard mask, p-SiOCH structures are exposed to in situ PET using different chemistries (NH_3, H_2, CH_4 or O_2) in a dual frequency capacitive reactor. The NH_3, H_2, CH_4 or O_2 treatments are first optimized on blanket wafers with the objective to minimize p-SiOCH modifications, i.e mainly methyl depletion and moisture uptake.

After etching in CF_4 / C_4F_8 / N_2 / Ar plasma, chemical topography analyses by XPS show the presence of a fluorocarbon (FC) layer on the p-SiOCH sidewalls. The FC layer is always removed whatever the post-etching plasma treatments and the surface of p-SiOCH sidewalls trenches is carbon and nitrogen rich after the CH_4 based PET and SiOF like after the NH_3, H_2 and O_2 PETs. The HF decoration technique and EP (with water used as solvent) show that the modified surface of the sidewalls is hydrophilic (thickness of the modified sidewall layer is between 15 and 20 nm) after the NH_3, H_2 and O_2 PETs while only a slight modification of the pattern sidewalls is detected after CH_4 based PET (less than few nanometers). The mechanisms leading to the p-SiOCH sidewall modification (pore sealing, methyl depletion...) induced by the plasma will be analyzed through the EP and FTIR analyses . The capabilities of such post-etching plasma treatments to prevent the barrier diffusion into p-SiOCH will be also discussed.

10:00am **PS1-MoM6 Reaction Mechanism and Profile Evolution for Porous Low-*k* Dielectric Sealing by Combined He and NH_3 Plasma Treatment**, ***J. Shoeb***, Iowa State University, *M.J. Kushner*, University of Michigan

Porous dielectric materials offer lower capacitance that reduces RC time delay in integrated circuits. While porosity of the dielectric can be as high as 0.5, the pores open to the surface which are internally connected can offer pathways for reactive species to enter into the porous network resulting in a degraded dielectric constant. The porous *low-k* materials are typically SiOCH – silicon dioxide with carbon groups, principally CH_3, lining the pores. Reactions with the CH_x groups can increase the *k* value of the material. To maintain the *low-k* value of porous dielectrics, sealing of the surface pores is desirable. Treatment of the porous material with successive He and NH_3 plasmas has been successful in sealing the pores[1]. The He plasma can break Si-O bonds creating dangling bonds on the SiO_2 surface while knocking off H atoms from CH_3 group which is connected to Si of SiO_2 by a Si-C bond. This creates more reactive CH_x ($x = 1,2$) species without significant damage to the substrate. Successive NH_3 plasma treatment seals the pore as NH_x ($x=0,1,2$) species passivate previously produced Si forming Si-N bonds and reactive CH_x groups adsorbing NH_x species to form C-N bonds. A reaction mechanism has been developed for the sealing of a porous carbon doped silica films (SiOCH) in sequentially applied He and NH_3/Ar plasmas. The HPEM (Hybrid Plasma Equipment Module) was employed to obtain the ion energy and angle distributions of reactive fluxes from inductively coupled plasmas. These are used as input to the MCFPM (Monte Carlo Feature Profile Module) with which profiles of the low-*k* materials after the plasma exposures are predicted. Results will be discussed, including validation with data from the literature, for the densification and sealing of pores as a function of pore radius, porosity, interconnectivity, bias voltage and plasma power.

1. A. M. Urbanowicz, et al., Electrochem. Solid-State Lett. **10**, G76 (2007).

* Work supported by Semiconductor Research Corp

10:40am **PS1-MoM8 Materials Interactions as a Challenge for BEOL RIE at 22nm Node and Beyond**, ***Y. Yin***, *J.C. Arnold*, IBM, *K. Zin, C. Chu, Y. Feurprier,* Tokyo Electron Limited, Japan, *Y. Mignot,* STMicroelectrics, *M. Sankarapandian, J. Chen, X. Liu*, IBM

As feature critical dimension (CD) shrinks toward the 22nm node and beyond, many problems become serious challenges for BEOL plasma patterning. Dimensionally, as pitch size reaches 100nm or below, pattern breakdowns due to resist delamination, mask wiggling and dielectric flopover have been observed. One of the root causes is the high Aspect Ratio (AR) of mask/dielectric lines. Two of the most significant mechanisms, mask flopover and dielectric flopover, occur during the plasma etching process. In the event of former, the soft organic materials in the litho stacks can bend over and lead to mask flopover when the AR is high. This flopover partially shadows the trench and forms distorted dielectric lines. In the later case, the dielectric lines themselves 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 flopover due to capillary forces. Pattern profile control during BEOL RIE is another major concern and needs to be addressed in order to improve product yield and reliability. In particular, low-k material sidewall damage and trench bottom roughening during RIE need to be improved for better profile control. Moreover, characterization of feature profiles at 22nm node and beyond is a significant challenge. In this paper, the RIE efforts on pattern wiggling/flopover, pattern profile control and profile characterization will be addressed.

This work was performed by the Research Alliance Teams at various IBM Research and Development facilities.

11:00am **PS1-MoM9 Challenges in Porous Ultra Low-k for 22nm Dual Damascene Trench Etch**, ***Q. Zhou***, *R. Patz, A. Darlak, J. Pender, M. Armacost,* Applied Materials, Inc., *C. Labelle,* GLOBALFOUNDRIES, *D. Horak*, IBM Research

The development of 32nm technology processes highlighted many issues associated with Ultra Low-K (ULK) material. The softness and porosity of ULK caused many challenges, such as etch front roughness and strip damage, requiring modifications to the etch chemistry, pressure regime and plasma density. This learning has been applied to the 22nm node but new issues have developed. As we go to sub-100nm pitch features, there appears to be a critical dimension where the microloading increases dramatically. Traditional methods of correcting this response, such as pressure, bias power and degree of polymerization modifications, are not as effective for these small feature sizes. Adding to the difficulty of solving this issue is the restriction put on the available process regime by other ULK concerns, e.g. etch front roughness, faceting, film damage, etc.. Microloading trends, and strategies for improving it, have been identified and will be presented. A second issue encountered at sub-100nm pitch involves multi-layer photoresist patterning. As feature size shrinks the aspect ratio of the masking material increases. If the aspect ratio is high enough, and the process conditions are not managed correctly, pattern flop-over has been observed. Proper management of the etch steps can help mitigate flop-over, but there is a limited process window. Some of the issues surrounding this phenomenon will be discussed.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

11:20am **PS1-MoM10 Sidewall Roughness Transfer during Advanced Interconnect Patterning: Impact of Masking Strategies and Plasma Etching Processes**, ***J. Ducote***, STMicroelectronics, France, *T. David, N. Posseme,* CEA-LETI-MINATEC, France, *T. Chevolleau,* LTM-CNRS, France, *A. Ostrovsky,* STMicroelectronics, France, *M. Guillermet,* CEA-LETI-Minatec, France, *F. Bailly,* STMicroelectronics, France, *E. Pargon, R. Inglebert,* LTM-CNRS, France, *C. Verove,* STMicroelectronics, France, *O. Joubert*, LTM-CNRS, France

As copper lines are continuously scaling down, the biggest issue we are facing today is the copper resistivity increase due to the scattering effect at the grain boundaries and surface. Recent study has proved that this behavior is potentially associated with the sidewalls roughness of the lines also leading to an increase of the time dependent dielectric breakdown [1].

Starting from an initial line width roughness (LWR) printed in the photoresist after the lithography step, we have investigated the impact of the etching chemistries on the LWR transfer in a damascene structure as a function of the hard mask strategy (metallic or organic).

To monitor the LWR variation, a three-dimensional critical dimensions-atomic force microscope (CD-AFM) from Veeco has been used. This technique allows reconstruction of the trench profiles of the patterns and measurement of the LWR along the trenches. However such analyses require the development of a specific protocol to determine the LWR after porous SiOCH integration in a dual damascene architecture.

In order to avoid any consumption or sticking of the AFM tip, it is mandatory i) to use a tip with a high stiffness and ii) to measure the LWR of the damascene structures after the etching and wet cleaning. The line width roughness measurements are performed on 100 scan lines over a scan length of 2 µm with a tip diameter of 100 nm and tip edge of 20nm, allowing a measurement accuracy of less than 1 nm.

We have investigated the impact of the two masking strategies investigated (titanium nitride (TiN) versus organic) and different etching chemistries (used for BARC open, TiN open and dielectric etching) on the LWR transfer by monitoring the LWR variation between LWR on photoresist trenches and LWR on p-SiOCH trenches.

No impact of the different chemistries investigated has been observed with a TiN hard mask. The initial LWR on the photoresist patterns (~6nm) remains almost constant after porous SiOCH lines etching. The comparison of the transfer of sidewalls roughness between a TiN and an organic mask will be also presented.

[1] E. Soda et al., JVSTB, 27(2), 2009, pp649

11:40am **PS1-MoM11 Post Etch Treatments as Solution to Limit or Prevent Residue Growth on Metallic Hard Mask after Porous SiOCH Etching in Fluorocarbon Based Plasma**, ***N. Posseme***, CEA-LETI-MINATEC, France, *R. Bouyssou, T. Chevolleau,* LTM-CNRS, France, *T. David,* CEA-LETI-MINATEC, France, *V. Arnal, C. Verove,* STMicroelectronics, France, *O. Joubert*, LTM-CNRS, France

For 45 nm interconnect technology node, porous SiOCH (p-SiOCH) materials are being introduced, leading to complex integration issues due to their high sensitivity upon etching and ashing plasmas exposure . Metallic hard mask (MHM) integration avoids exposure of the porous film to plasma stripping processes but generate its own issues such as metal contamination on patterned structures (leading to line and via opens, strongly impacting the yield performance).

In this work, we have investigated the efficiency of *in situ* post-etch plasma treatments (PET) such as NH_3, CH_4, O_2 and H_2 to limit or prevent residues formation.

First, the experiments have been performed on TiN blanket wafers deposited on 200 nm thick SiO_2 layers. The TiN layer has been exposed to conventional fluorocarbon (FC) based chemistry and PET in an industrial dual frequency capacitively coupled plasma etcher. Different analyses techniques such as scanning electron microscopy (SEM) and ex-situ x-ray photoelectron spectroscopy (XPS) have been used in order to analyze the presence of metal residues and have a better understanding of the residue formation mechanism .

After FC etching and atmosphere exposure, a huge density of residues is observed, correlated with the presence of significant fluorine concentration (33%) on the TiN surface. The mechanism of metallic residues formation on the metallic hard mask has been clearly identify as a reaction between fluorine and air moisture (forming HF acid) and the oxidized metal to form a metallic salt.

H_2, O_2, and NH_3 PET strongly reduce the density of residues by partially removing fluorine on the TiN surface (8-13%). With the CH_4 PET, no more residues are observed despite an important fluorine concentration (28%) remaining on the surface. The residue removal is explained by the formation of a thin carbon passivation layer on top of the TiN surface preventing reactions between fluorine and air moisture.

Furthermore, a complementary study has been performed on patterned wafers using trench first MHM integration with a PECVD p-SiOCH dielectric (porosity of 20%, k=2.5). The implementation of the post-etch plasma treatment show that the residues density on MHM strongly depends on the etching chemistry with H_2, O_2, NH_3 while with CH_4, the efficiency in preventing residues formation is not chemistry dependent. The implementation of such PETs using a MHM and a porous SiOCH has been successfully integrated with an improvement of the electrical performances.

Plasma Science and Technology
Room: A8 - Session PS2+PV-MoM

Plasma Processing for Photovoltaics
Moderator: T.A. Gessert, National Renewable Energy Laboratory

8:40am **PS2+PV-MoM2 Plasma Etching and Texturing of Multi-Crystalline for Silicon Solar Cells using Remote-Type Pin-To-Plate Dielectric Barrier Discharge**, ***J.B. Park***, *J.S. Oh, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

During the preparation of the wafers for the multi-crystalline silicon (mc-Si) solar cells, the mechanical saw damage induced during the slicing of mc-Si ingots into wafers needs to be removed by etching in addition to the texturing of the silicon surface for the increased light scattering. For the etching and texturing of the mc-Si substrates, isotropic wet processing by using alkaline or acid solution is generally applied, however, wet treatments are environmentally undesirable due to the large amount of chemicals used.

In this study, an atmospheric pressure plasma called “remote-type pin-to-plate DBD” was used for the application to the etching of the saw damage removal and texturing process of mc-Si to increase the processing rate by increasing the plasma density without damaging the substrate surface. Especially, the effect of additive gases such as NF_3 and O_2 to the N_2-based atmospheric pressure plasma on the etching and texturing characteristics of mc-Si was investigated.

The results showed that the addition of NF_3 up to 1 slm increased the mc-Si etch rate continuously by increasing the F radicals in the gas mixture. Furthermore, the addition of a certain amount of O_2 (400sccm) to the mixture of N_2(40 slm) /NF_3(1slm) increased the mc-Si etch rate further by showing the two times higher etch rate of mc-Si (749.6 nm/scan, 1meter/scan). Especially, the addition of O_2 to the N_2/NF_3 improved the surface morphology by increasing surface texturing and, by the addition of 600sccm O_2, the reflectance less than 20% could be obtained.

9:00am **PS2+PV-MoM3 Production of Crystalline Si Nanoparticles for Third Generation Photovoltaics using a Multi-Hollow Discharge Plasma CVD Method**, ***Y. Kawashima***, *H. Sato, K. Koga, M. Shiratani*, Kyushu University, Japan, *M. Kondo*, AIST, Japan

Novel solar cells employing multiple exciton generation (MEG) are attracting much attention as third generation solar cells of high efficiency above 20%. For the MEG, an energetic exciton is generated in a semiconductor nano-crystal by a high energy photon more than twice as large as the band gap of the nano-crystal. Subsequently, the energetic one produces another in the nano-crystal by the inverse Auger process [1]. An issue for realizing the MEG solar cells is production of size-controlled crystalline Si nanoparticles. We have produced crystalline Si nanoparticles of 1 nm in size using a multi-hollow discharge plasma CVD method [2]. For the multi-hollow discharge plasma CVD method, discharges are sustained in small hollows of 5 mm in diameter. Crystalline nanoparticles are nucleated and grow in the discharges of SiH_4+H_2 (>99.5%) and then they are transported to the downstream region by gas flow. Their size is limited up to a few nm in size due to a short gas residence time in hollows. Nanoparticles are collected by stainless mesh grids located at the downstream region. They are dispersed in methanol to measure their photoluminescence. The excitation laser wavelength is 244nm or 405nm. For 405nm light irradiation,the photoluminescence spectrum has a peak at 490nm (2.53eV), corresponding to the bandgap of the Si nanoparticles of 1 nm in size. For 244nm light irradiation, the spectrum has a 380nm (3.27eV) peak corresponding to recombination centers at their surface as well as a 484nm (2.56eV) peak corresponding to their bandgap. These experimental results demonstrate generation of excitons in the Si nanoparicles. Si nanoparticles produced may be applicable as a material for MEG solar cells. We also have measured absorption spectrum of Si nanoparticles dispersed in methanol. Si nanoparticles show stronger light absorption at the shorter wavelength (<250 nm). To realize MEG solar cells, fabricating nanoparticles of an optimaized size for MEG in large quantity is important.

[1] A.J.Nozik, Physica E **14**, (2002)115.

[2] T. Kakeya, Kazunori Koga, Masaharu Shiratani, Yukio Watanabe, Michio Kondo, The Solid Films, **506-507**, (2006)288.

9:20am **PS2+PV-MoM4 Novel Model-Based Sensor for Thin Film Deposition on Large Area Substrates**, *M. Klick*, Plasmetrex, Germany, ***L. Eichhorn***, *R. Rothe*, Plasmetrex

Large area plasma coating becomes more important with increasing diameter of semiconductor wafers and thin film Si solar cells. The layer characteristics as uniformity of films produced by capacitive RF plasmas depends on effects as the standing wave and skin effect.

A reduced plasma physical model in the novel sensor is used to describe special features of large area and capacitive RF plasmas. It involved dynamic electron effects by a fluid model for the plasma bulk and nonlinear mechanisms by a nonlinear sheath model - called it Nonlinear Extended Electron Dynamics (NEED).

It involves also the nonuniformity and nonlinearity of the plasma sheath in the front of the substrate electrode, large electrode area, and medium pressure. The model provides also the dependence of the Fourier spectrum of the local RF current on the plasma density and the electron collision rate. Only lower harmonics of the RF current can be observed at medium pressure (100 Pa – 1000 Pa). Depending on the amount of harmonics of the local RF current used, it can be utilized also to estimate important plasma parameters as the electron collision rate and the ratio of the excitation frequency to the resonance frequencies of the spatial modes is found to determine the nonuniformity caused by the standing wave. The skin depth can be estimated as well to show the influence on spatial distribution of the RF current.

The major advantage is the real time, robust, and non-intrusive characterization of large area plasmas. An additional feature is the easy calculation of the plasma sheath voltage distribution at the grounded counter electrode. Both is mandatory to understand and to control the deposition rate distribution in particular for large area RF plasmas. So cost-efficient virtual metrology can substitute partially the expensive and time intensive real metrology.

9:40am **PS2+PV-MoM5 Plasma Processing of Thin Silicon Films for Photovoltaic Applications**, ***A.H.M. Smets***, National Institute of Advanced Industrial Science and Technology, Japan and Eindhoven University of Technology, Netherlands, *M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands, *T. Matsui, M. Kondo*, National Institute of Advanced Industrial Science and Technology, Japan **INVITED**

Hydrogenated amorphous silicon (a-Si:H) and hydrogenated microcrystalline silicon (μc-Si:H) are thin film silicon phases which are generally deposited at low processing temperatures by means of plasma enhanced chemical vapour deposition (PECVD) using hydrogen diluted silane gas mixtures. The lattice of dense a-Si:H is best described by a vacancy rich network (1-2 %) which lacks any medium and long range order, whereas the lattice of μc-Si:H consists of crystalline silicon grains (few nm’s up to microns) imbedded in to an amorphous network or tissue. One hot application of these films is the integration in to thin silicon film photovoltaic devices. In comparison to a-Si:H phase, the μc-Si:H phase has the advantage of an enhanced spectral response in the red part of the solar spectrum and a better opto-electronic stability under illumination.

Since the deposition of the μc-Si:H phase under low processing temperatures (~160-250 °C) is obtained by increasing the hydrogen dilution in a silane plasma, it is believed that additional flux of atomic hydrogen at the surface enhances crystalline relaxation of the silicon atoms in the lattice during growth.

With respect to photovoltaic applications of μc-Si:H, high quality material is classified as dense material without any significant post-deposition oxidation, as oxidation is linked to a reduction in the red response of the *p-i-n* solar device. This specific μc-Si:H phase has the following properties: 1) crystalline grains with a preferentially [220] oriented growth, 2) has no crystalline grain boundaries, as these internal surfaces have been identified as the location at which the unwelcome post-deposition oxidation occurs and 3) is deposited close to conditions in which the growth transfers from amorphous to microcrystalline.

In this contribution we will address in detail the material properties of μc-Si:H and its relation to its performance in solar cells, the growth mechanism of the μc-Si:H phase under plasma deposition conditions and the crucial role of the control of plasma processing in obtaining device grade material. Finally, we will discuss the upscaling of the deposition technology (high deposition rates over large areas), which is an important issue in substantially reducing the cost-price of thin silicon photovoltaic products. We will present the recently explored deposition regime at higher processing pressures (~5-25 Torr), which has a high potential to bring about this important breakthrough in the thin silicon film photovoltaic technology.

10:40am **PS2+PV-MoM8 Atomic Hydrogen Induced Defect Kinetics in Hydrogenated Amorphous Silicon: An In Situ Real Time Study**, ***M.C.M. van de Sanden**, F.J.J. Peeters,* Eindhoven University of Technology, The Netherlands*, J. Zheng,* Peking University, China*, I.M.P. Aarts,* ASML, The Netherlands*, A.C.R. Pipino,* Tanner Research*, W.M.M. Kessels*, 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 20-80 nm a-Si:H films were grown on the Total Internal Reflection (TIR) surface of a folded miniature optical resonator by thermal decomposition of silane on a hot filament. Measurements are performed over a temperature range of 80 – 200 ºC. The observed changes in the optical loss during H dosing of a-Si:H are attributed to the creation and healing of sub-gap Dangling Bond (DB) defect states and were measured with a sensitivity of ~ 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 decreases with temperature. 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. Due to their limited lifetime the created DB defects are identified as the result of H insertion into strained Si-Si bonds in the bulk material. Extensive kinetic modeling of this process is used to determine activation energies for the hydrogen-material interactions and DB formation in a-Si, which are of key importance in a-Si:H thin film solar cells. Moreover the implications of this study for Eley-Rideal type reactions on the surface and hydrogen exchange reactions in the bulk will be addressed.

11:00am **PS2+PV-MoM9 Hydrogen-dominated Plasma, Due to Silane Depletion, for Microcrystalline Silicon Deposition**, ***A.A. Howling**, R. Sobbia, Ch. Hollenstein*, EPFL Lausanne, Switzerland **INVITED**

Plasma conditions for microcrystalline silicon deposition generally require a high flux of atomic hydrogen, relative to SiH_x radicals, on the growing film. The necessary dominant partial pressure of hydrogen in the plasma is conventionally obtained by hydrogen dilution of silane in the flow inlet. However, a hydrogen-dominated plasma environment can also be obtained due to plasma depletion of the silane in the gas mixture, even up to the limit of pure silane inlet flow, provided that the silane depletion is strong enough. At first sight, it may seem surprising that the composition of a strongly-depleted pure-silane plasma consists principally of molecular hydrogen, without significant contribution from the partial pressure of silane radicals. The aim here is to bring some physical understanding by means of a zero-dimensional, analytical plasma chemistry model. The model is appropriate for uniform, large-area showerhead reactors as shown by comparison with results of three-dimensional numerical simulations. The SiH_x densities remain very low because of their rapid diffusion and surface reactivity, contributing to film growth which is the desired scenario for efficient silane utilization. Significant SiH_x densities due to poor design of reactor and gas flow, on the other hand, would result in powder formation wasting silane. Conversely, hydrogen atoms are not deposited, but associate on the film surface and re-appear as molecular hydrogen in the plasma. Therefore, in the limit of extremely high silane depletion fraction (>99%), the silane density falls below the low SiH_x densities, but only the H radical can eventually reach significant concentrations in the hydrogen-dominated plasma.

11:40am **PS2+PV-MoM11 Plasma Uniformity Measurements in a Scalable, Multi-Electrode, VHF/UHF Plasma Source**, ***D. O'Farrell**, A.R. Ellingboe, S. Linnane, C. Gaman*, Dublin City University, Ireland

The ability to deposit large area thin film amorphous silicon films using PECVD is of significant interest in a number of fields including photovoltaics and flat panel display. The desire to deposit larger area films faster has lead to a recent push towards the use of VHF/UHF frequencies which result in faster deposition rates but also result in significant film non-uniformities due to wavelength effects even over relatively small areas. Several methods have been employed in an attempt to overcome these non-uniformity issues but many barriers still exist when it comes to wide scale application. In this work a scalable, multi-electrode, VHF/UHF plasma source is described which aims to resolve these issues. Data is presented demonstrating plasma uniformity over the source for a series of powers, pressures and operating frequencies. Different operating regimes are discussed.

Advanced Surface Engineering
Room: B1 - Session SE1-MoM

Photocatalytic Coatings
Moderator: H. Barankova, Uppsala University, Sweden

8:20am **SE1-MoM1 Development of Highly Functional Visible Light-responsive TiO_2 Thin Film Photocatalyst Materials by a RF Magnetron Sputtering Method and their Applications for our better Environment and Production of Clean Energies using Sunlight***, M. Anpo, M. Matsuoka, **M. Takeuchi***, Osaka Prefecture University, Japan **INVITED**

Titanium oxide-based catalysts have attracted a great deal of attention for their application in photocatalytic materials with high reactivity, thermal stability and nontoxic properties[1)]. However, unlike natural photosynthesis in green plants, they can make use of only 3-4% of solar light, necessitating the use of a UV light source. Recently, we have successfully applied a RF magnetron sputtering deposition method to design unique and efficient titanium oxide photocatal ysts which enable the absorption of visible light of longer than 550 nm. These newly developed titanium oxide catalysts were found to work as environmentally-friendly photocatalyst, leading to the efficient use of solar energy for the production of clean H_2 and O_2 from water with a separate evolution and other significant reactions[2-4)].

In the present lecture, the results obtained for the photocatalytic decomposition of H_2O with the separate evolution of H_2 and O_2 under sunlight irradiation of the visible light-responsive titanium oxide thin film photocatalysts will be presented.

References

1) M. Anpo, et al., in "*Annu Rev. Mater. Res.*", Eds. J. M. Thomas and P. L. Gai, **35**, 1 (2005).

2) M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, et al., *Catal. Today*, **120**, 133 (2007).

3) M. Kitano, M. Matsuoka, J. M. Thomas, M. Anpo, et al., *Top. Catal*., **49**, 24 (2008).

4) S. Fukumoto, M. Kitano, M. Takeuchi, M. Matsuoka, M. Anpo, *Catal. Lett.*, **127**, 39 (2009).

9:00am **SE1-MoM3 The Effect of Nb Additions on the Synthesis, Photo-Response, and Photo-Activity of TiO_2 Thin Films***, **P.A. DeSario**, M.E. Graham, K.A. Gray*, Northwestern University

A deeper understanding of the relationships between synthesis, structure and function is needed to improve the design of materials tailored to solar energy conversion and storage. The objective of this research is to synthesize TiO_2 composites with properties tailored to the harvesting and conversion of solar energy. Unbalanced reactive dc magnetron sputtering 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 ($Ti_{1-x}Nb_xO_2$) in the range of $0<x<0.45$ to evaluate the effect of cation doping on optical, chemical and physical properties. The films were interrogated structurally and functionally using SEM, EDX, XPS, AFM, UV-Vis absorption spectroscopy, and XRD. Selected films were evaluated with respect to gas phase CO_2 reduction and gas phase oxidation of acetaldehyde and the action spectra were determined.

Improvements in catalytic efficiency can be made by shifting the photoresponse of tiania-based materials to utilize a larger portion of the solar spectrum. Many attempts have been made to red-shift the photoresponse of TiO_2 through cation doping or anion doping. It is not yet proven, however, if the shift in photoresponse correlates to enhanced photoactivity under visible light or simply the creation of color centers. Preliminary findings show that Nb doping enhances oxidative reactivity under visible light. Reductive chemistry does not seem to be enhanced, however, which suggests how Nb substitution is altering band gap structure.

While earlier work established the relationships between sputtering process parameters and the film structure, including phase identity and distribution in pure TiO_2, this work is focused on how the addition of Nb cations 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. 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 Nb additions shift the regions of phase stability compared to pure TiO_2 and favor the growth of rutile. The shift in optical absorption to the visible wavelength range as a function of Nb concentration and anatase-rutile phase distribution is also presented.

Our work on pure TiO_2 indicates that the films with the highest photoreactivity were nanocrystalline, mixed phase structures (~70% anatase) with substoichiometric oxygen concentration. Results are presented comparing the photoreactivity of the Nb doped films with the pure TiO_2 mixed phase films of similar structure and phase proportions.

9:20am **SE1-MoM4 Identification of Carbon Sensitization for the Visible Light Photocatalytic Titanium Oxide***, **Y. Chen**, G. Jhan, G. Cai, T. Lin, M.S. Wong, C. Cheng*, National Dong Hwa University, Taiwan

Titania nanopowders synthesized by low-pressure flat-flame metalorganic chemical vapor condensation method are known to possess visible light photocatalytic ability even they are produced without intentional doping. While the visible-light absorption of the powder is convincing, the cause of visible light absorption is still inconclusive. There are 3 main possible causes for visible light absorption discussed earlier. First is the anatase/rutile interface that generates defect levels for visible light absorption. Second is the nitrogen doping that forms the absorption center. Third is the carbon doping that forms the absorption center. In order to confirm that carbon doping is the major cause for the visible light absorption of the powder, we modify the process using helium in place of nitrogen to eliminate the nitrogen doping possibility. Helium in place of nitrogen is used as the titanium precursor carrier gas, where the precursor is titanium isopropoxide. 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. From the methylene blue decomposition study we found that the powder synthesized under low precursor feed rate possesses high photocatalytic efficiency under illumination of visible light. Since nitrogen is avoided in the process, the visible light absorption cannot be due to nitrogen doping. We also found that the nanopowder formed has a single phase of anatase. Thus the nanopowder does not have anatase/rutile interface, and we can eliminate the possibility of visible light absorption by the anatase/rutile interface. The visible light absorption should thus be resort to the carbon doping. XPS studies show the presence of several carbon related bonds except Ti-C bond. This suggests that the carbon does not incorporate into the TiO_2 crystal and should locate on the surface of the nanopowder. Thus the carbon species act as a visible light sensitizer for the titania as a photocatalyst. Among all carbon bonds the C-C bond is believed to be responsible for the light absorption, since all other carbon related bonds are not chromophores. The carbon should be in the cluster form to become colored. The visible light TiO_2 photocatalysis induced by carbon doping is confirmed and explained.

9:40am **SE1-MoM5 Effects of Oxygen Vacancies on Electro-Optic Properties of Reactively Co-Sputtered Nb-doped Titania Films***, H.C. Hsing, H.T. Chang, T.Y. Lu, C.C. Mo, **M.S. Wong***, National Dong Hwa University, Taiwan

Transparent conducting niobium-doped titania was prepared by reactive co-sputtering of Ti and Nb metal targets in oxygen and argon plasma. The as-deposit films were annealed at 650℃ under air atmosphere for 8 hr and then hydrogen annealed. Two different H_2-annealig procedures were executed to generate different concentration of oxygen vacancies: the H_2-annealing time ranges from 10 min to 4 hr under constant temperature and H_2-annealing temperature ranges from 200℃ to 800℃ under constant time. From the XPS spectra, the concentration of oxygen vacancies was observed, and directly affects the carrier concentrations in the thin film. The thin film's structure and optical properties was also measured and discussed.

10:00am **SE1-MoM6 Micro-Structure of Photo-Catalytic TiO_2 Films Deposited by Oxygen Ion Assist Reactive Evaporation Method and Reactive Sputtering***, **Y. Hoshi**, D. Ishihara, H. Lei, T. Sakai*, Tokyo Polytechnic University, Japan

TiO_2 films were deposited on glass slide substrates by using oxygen ion assist reactive evaporation method(IARE) and reactive sputtering method(RS), and their micro-structure was investigated by using FE-TEM.

The films of above 1um thick deposited by IARE at the substrate temperature of 300 ℃ and ion accelerating voltage of 200 V has excellent photo-catalytic properties. However, the films with thickness lower than 1um shows poor photo-catalytic properties. In these films, the crystallization in the initial layer on the substrate was suppressed so that the film near the substrate contains large amount of amorphous phase. As the film grew, crystallization was enhanced and clear columnar structure was developed in the films. As a result, most of the amorphous phase was disappeared at the thickness above 600 nm. In addition, the column were separated each other with clear spaces at the thickness above 800 nm. This may be the reason why the photocatalytic properties improved significantly as the film thickness increased above 1um. These results suggest that the poor crystal structure is the main reason why the film with thickness below 800nm has poor photo-catalytic properties.

On the other hand, compared with the films deposited by IARE, crystallization was enhanced in the deposition of the films by using a reactive sputtering. As a result, crystallized film with thickness below 200 nm can be obtained at 300 ℃. This may be due to the fact that the depositing atoms in the sputtering process have much larger kinetic energy than in IARE. The film, however, has much dense structure and smooth surfaces, which results in a poor photo-catalytic organic decomposition properties.

10:40am **SE1-MoM8 Enhancement of Visible-Light Activities of Photocatalytic WO_3 Films Deposited by Sputtering***, **A. Murata**, M. Kikuchi, N. Oka, Y. Sato, S. Nakamura, H. Yamaguchi, Y. Shigesato*, Aoyama Gakuin University, Japan

We have been reported on photoinduced superhydrophilicity and oxidative decomposition of organic compounds under visible light irradiation on polycrystalline WO_3 films deposited by reactive magnetron sputtering at the substrate temperature at 800 ^{o}C [1,2,3]. On the other hand, Abe, et al. reported that WO_3 powder loaded with Pt nanoparticles exhibits high efficiency for the decomposition of organic compounds under visible light irradiation, certainly due to promotion of multielectron O_2 reduction [4].

In this study, we deposited the photocatalytic WO_3 films with visible-light-activity on fused silica glass substrates by dc reactive magnetron sputtering using a W metal target. The substrate temperatures and total gas pressure during the deposition were 800 ^{o}C and 5.0 Pa, respectively. In addition, Pt was deposited on WO_3 film surfaces at RT by sputtering with various sputtering power and deposition time. In the case of Pt deposited on WO_3 films, 3D growth mode (Volmer-Weber) should be expected in general, because atoms or molecules in the deposit are more strongly bound to each other than to the substrate. The surface coverage of Pt on the WO_3 films were estimated by X-ray photoelectron spectroscopy (XPS), which implied that the Pt film followed Volmer-Weber type film growth process, i.e., after an initial nucleation, an island structure grew and coalesced with each other with increasing film thickness. High resolution electron microscopy (HREM) revealed that Pt nano-particles with diameter of about 2 nm were generated at the early stages of the Pt film growth, which dispersed uniformly on the columnar polycrystalline WO_3 films possessed of large surface area.

The photocatalytic activity was evaluated by photodecomposition of acetaldehyde under the irradiation of visible light (Xe lamp with a 410-500 nm band pass filter, 1.0 mW/cm^2). With increasing in the Pt deposition time upto 10 sec, the decomposition rates for the Pt loaded WO_3 films were higher than that on the pristine WO_3 film. Especially, for the WO_3 films deposited with the Pt by 7 sec, acetaldehyde was completely decomposed within 150 min, on which the surface coverage of Pt indicated about 60%.

[1] M.Ebihara, Y.Shigesato,et al., Proceedings of the 3rd ICCG (2000) 137.

[2] M. Kikuchi, Y. Shigesato, et al., Abstract of the 21st IUPAC SYMPOSIUM (2006) 496.

[3] M. Kikuchi, Y. Shigesato, et al., Proceedings of the 6th ICCG (2006) .

[4] R. Abe, B. Ohtani, et al., J. Am. Chem. Soc. 130, (2008) 7780.

11:00am **SE1-MoM9 Optimization of Photovoltaic Performance through the Integration of Electrodynamic Dust Shield Layers***, **S. Nason**, K. Davis, N. Hickman,* Florida Solar Energy Center*, E. Arens, J. McFall, C. Calle*, Kennedy Space Center

The viability of photovoltaics on the Lunar and Martian surfaces may be determined by their ability to withstand significant degradation in the Lunar and Martian environments. One of the greatest threats is posed by fine dust particles which are continually blown about the surfaces. In an effort to determine the extent of the threat, and to investigate some abatement strategies, a series of experiments were conducted outdoors and in the Moon and Mars environmental chamber at the Florida Solar Energy Center .

Electrodynamic dust shield prototypes based on the electric curtain concept have been developed by our collaborators at the Kennedy Space Center [1]. These thin film layers can remove dust from surfaces and prevent dust accumulation. Several types of dust shields were designed, built and tested under high vacuum conditions and simulated lunar gravity to validate the technology for lunar exploration applications.

Gallium arsenide, single crystal and polycrystalline silicon photovoltaic integrated devices were designed, built and tested under Moon and Mars environmental conditions as well as under ambient conditions. Photovoltaic efficiency measurements were performed on each individual cell with the following configurations; without an encapsulation layer, with a glass covering, and with various thin film dust shields. It was found that the PV efficiency of the hybrid systems was unaffected by these various thin film dust shields, proving that the optical transmission of light through the device is virtually uninhibited by these layers.

The future goal of this project is to incorporate a photovoltaic cell as the power source for the electrodynamic dust shield system, and experimentally show the effective removal of dust obstructing any light incident on the cell, thus insuring power production is maximized over time.

[1] C.I. Calle, C.R. Buhler, J.G. Mantovani, S. Clements, A. Chen, M.K. Mazumder, A.S. Biris, A.W. Nowicki, Electrodynamic dust shield for solar panels on Mars, Lunar and Planetary Science XXXV, 2004, p. 2014.

Advanced Surface Engineering
Room: C4 - Session SE2-MoM

Pulsed Plasmas in Surface Engineering
Moderator: J. Patscheider, EMPA, Switzerland

8:20am **SE2-MoM1 Industrialization of Metal Ion Sputtering**, ***R. Cremer***, KCS Europe **INVITED**

Since its introduction by Kouznetsov et al. in 1999, the HIPIMS technology has seen a remarkable rise in interest from both academic and industrial viewpoint. Although the high ionization of the plasma and the resulting advantages for industrial sputter applications have been verified more than a decade ago, industrial usage of the metal ion sputtering technology has been limited due to various technical drawbacks.

Only recently, a various number of authors have reported the overcome of the hitherto existing disadvantages of the technology like low deposition rate, biasing issues, arcing and reliability of the technology.

This paper gives an overview on the industrialization of metal ion sputtering in various applications. Special focus will be given to the comparison of ionization in different coating technologies like sputtering, metal ion sputtering, arc ion plating and thermionic arc evaporation. The paper will also comment on future options and limitations of industrial metal ion sputtering.

9:00am **SE2-MoM3 Structural and Mechanical Behavior of Fullerene-Like and Amorphous Carbon Nitride Thin Films Deposited by HPPMS**, ***S. Schmidt***, *G. Greczynski,* Linköping University, Sweden*, E. Broitman,* Carnegie Mellon University*, L. Hultman*, Linköping University, Sweden

The structural and mechanical properties of fullerene-like (FL) and amorphous carbon nitride (CN_x) films were deposited using High power pulsed magnetron sputtering (HPPMS) in an industrial CC-800/9 CemeCon chamber and compared with films deposited by DC magnetron sputtering mode of operation.

Films of 1 µm and 2 µm thickness were grown on Si and steel substrates, respectively. Carbon nitride films were deposited via HPPMS from a high purity graphite target in an Ar/N_2 discharge at 400 mPa, the N_2 fraction varied from 0 to 0.5 and different substrate temperatures ranging from ambient temperature to 300°C were chosen. Furthermore, a novel HPPMS substrate pretreatment employing two HPPMS power supplies was used to optimize the adhesion of the films: the first power supply established the discharge; the second produced a pulsed substrate bias. The created Cr-plasma cleaned the substrate surface and formed a Cr-containing gradual interface into the substrate. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and transmission electron microscopy (TEM) were used to study the microstructure of both, the films and the interfaces. The hardness and the elastic recovery of the CN_x films were measured using nanoindentation. A deposition process window is demonstrated for the growth of dense fullerene-like (FL) film structures consisting of curved, frequently intersecting, and highly in-plane oriented basal planes.

9:20am **SE2-MoM4 Effects of the Working Pressure and Pulse Parameters on the Ion Energy and Mass Distributions in Modulated Pulse Power Sputtering Plasma**, ***W.D. Sproul***, Reactive Sputtering, Inc., *J. Lin, J.J. Moore, B. Mishra,* Colorado School of Mines*, J.A. Rees,* Hiden Analytical Ltd, UK*, Z.L. Wu, J. Wang,* Colorado School of Mines*, R. Chistyakov, B. Abraham*, Zond/Zpulser

The modulated pulse power (MPP) sputtering technique is a variation of high power pulsed magnetron sputtering (HPPMS) that generates a high ionization density plasma by manipulating the pulse shape, intensity, and duration. In this study, the time-averaged ion energy and ion mass distributions of the MPP plasma generated during sputtering a metal Cr target in pure Ar at different working pressures, pulse frequencies, and the strong ionization periods were investigated. The MPP plasma was studied using an electrostatic quadrupole plasma mass spectrometer which was installed parallel to the target surface in a closed field unbalanced magnetron sputtering system. It was found that an increase in the working pressure led to an increase in the peak ion flux and a decrease in the high ion energy tail. An increase in both the gas and metal ion species was observed as the pulse frequency was increased using the same pulse shape. Additionally, the effects of different combinations of the weak and strong ionization durations on the ion energy distributions of the gas and metal ion species will be reported.

10:00am **SE2-MoM6 Effects of HiPIMS Plasma Transport on Thin Film Deposition**, ***D. Lundin***, Linköping University, Sweden*, N. Brenning, M.A. Raadu,* Royal Institute of Technology, Sweden*, U. Helmersson*, Linköping University, Sweden

A new exciting development of magnetron sputtering was achieved when introducing high power impulse magnetron sputtering (HiPIMS). HiPIMS is one of the most promising improvements of common IPVD techniques and is already making its way to industrial applications. The HiPIMS plasma generates large quantities of ions of the sputtered material due to a high plasma density, but also acceleration of the ions increasing the bombardment of the growing film without using a substrate bias voltage. Also observed is a lower deposition rate for HiPIMS than that obtained for conventional DC sputtering, using the same average power. In order to optimize the process, controlling ion acceleration and increasing deposition rate, the mechanisms for transport of charged particles in this type of plasma need to be known. In the present work, it is shown that the electron mobility across the magnetic field is enhanced by typically an order of magnitude during the HiPIMS discharge compared to DC magnetron sputtering. This cannot be explained by classical theory of diffusion and electrical conductivity or Bohm diffusion. The transport is directly reflected by an anomalously low azimuthal-to-discharge current ratio, $J_\varphi / J_D = 2$. On the microscopic scale, the anomalous transport can be shown to be mediated by observed azimuthal electric field oscillations in the lower hybrid range. Furthermore, new insights from experimental data and plasma discharge modeling will be presented, which show that a large fraction of the ionized species are attracted back towards the target, either by electric fields in the bulk of the plasma, or by the stronger local fields in the cathode sheath. In this context, it is demonstrated that the effect of the anomalously high electron mobility to reduce the bulk **E** field is important to understand and control. The study also verifies that the resistive friction force, $\mathbf{F}_{i,\varphi}$, associated with the anomalous resistivity, can accelerate the ions azimuthally, as is shown both indirectly from changes in the deposition patterns, and directly by mass spectrometry.

10:40am **SE2-MoM8 Deposition Rates of High Power Impulse Magnetron Sputtering: Physics and Economics**, ***A. Anders***, Lawrence Berkeley National Laboratory **INVITED**

Deposition by high power impulse magnetron sputtering (HIPIMS) is considered by some as the new paradigm of advanced sputtering technology, yet this is met with skepticism by others for the reported lower deposition rates, if compared to direct current (DC) sputtering of equal average power. In this contribution, absolute and relative (normalized) deposition rates are compared, and the underlying physical reasons for differences are discussed, including (i) ion return for self-sputtering, (ii) the less-than-linear increase of the sputtering yield with increasing ion energy, (iii) yield changes due to the shift of species responsible for sputtering, (iv) change in plasma impedance and sheath voltage, (v) changes in film density, (vi) noticeable losses in the switch module, (vii) changes of the magnetic balance and particle confinement of the magnetron due to self-fields at high current, and (viii) superposition of sputtering and evaporation for selected materials. The situation is even more complicated in reactive systems where the target surface chemistry is a function of the discharge conditions. While generally these factors imply a reduction of the normalized deposition rate, increased rates have been reported for certain conditions. Finally, some points of economics and "value added" are considered.

This work was supported by the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

11:20am **SE2-MoM10 Optical Diagnostics of HIPIMS Discharges: Dependence of Film Growth on Control Parameters**, ***M. Lange***, UTC and AFRL/RXBT, *J. Jones,* AFRL/RXBT, *C. Muratore,* UTC and AFRL/RXBT, *A. Reed,* AFRL/RXBT, *A. Waite,* UTC and AFRL/RXBT, *A. Voevodin*, AFRL/RXBT

High power impulse magnetron sputtering is a physical vapor deposition process distinguished by its capability to produce a high flux of ionized target material incident upon growing film surfaces. This characteristic gives the process advantages over conventional dc sputtering in that the orientation and relative density of thin films can be controlled by modulating the energy of ions constituting the film material. Unfortunately, the deposition rate in HIPIMS is often lower than in standard magnetron sputtering when processes conducted with the same time-averaged power are compared. The deposition rates for HIPIMS processes are dependent upon the power waveforms to the target, as well as the ionization energy, self sputtering rate, atomic mass, and other physical properties of the sputter target material. Correlation of target materials with thoughtfully selected properties to resultant plasma characteristics can reveal the nature of these relationships. For example, the ionization energies of hafnium and titanium are similar (6.8 eV), but their atomic masses of 178 amu and 48 amu respectively, affect the deposition rate in addition to the temporal-spatial plasma distributions, which were measured here using optical and electrostatic diagnostics. Studies of these materials provide insight on the effect of target mass on ion transport and film growth rates. Substrate bias and pulse duration have also been shown to effect the optical emissions from the plasma generated during HIPIMS operation. Correlation of these plasma characteristics to the structure and properties of elemental and compound thin films will be presented.

11:40am **SE2-MoM11 Time-resolved Plasma Characterization in Modulated Pulse Power (MPP) Magnetron Sputtering**, ***A.N. Cloud***, *R.E. Flauta, M.J. Neumann, S.L. Rohde, D.N. Ruzic*, University of Illinois at Urbana-Champaign

High power impulse magnetron sputtering (HIPIMS/HPPMS) has attracted considerable attention from industry due its ability to produce thin films and features of excellent adhesion, superior density, decreased roughness, and extreme conformity. The intense pulsed plasma density – on the order of 10^{18} m^{-3} – provides a large concentration of metal ions that can be used to produce high-quality, homogeneous coatings. The high ionization fraction at the substrate allows for fine control of the sputtered species during deposition.

Modulated pulse power (MPP) can be employed to shape an arbitrary voltage waveform that is applied to the cathode. This programming freedom allows control over pulse duration, intensity, duty cycle, and average power. Voltage oscillations during the 1.0 – 3.0 ms pulse on the order of 25-65 kHz induce instabilities in the plasma discharge that may have a marked effect on the level of ionization within the discharge and distribution of the metal ions. The oscillation frequency range corresponds to the expected ion cyclotron angular frequencies. Past investigations of MPP have only revealed time-averaged plasma parameters, but knowledge of events during the pulse is required to further understanding of the physical mechanisms involved.

MPP discharges produced with a 1000 cm^2 circular planar magnetron were characterized. A gridded energy analyzer and quartz crystal microbalance were used to measure a higher ionization fraction than with conventional magnetron sputtering under a variety of deposition conditions. Nominal values of approximately 6% were attained for the sputtering of titanium at power densities as low as 100 W/cm^2. The energy spectrum and flux of these ions at the substrate location were also measured, finding the incident metal ions to be of low energy between 1 and 4 eV. Time-resolved plasma properties including saturation current, electron temperature, and density are measured and mapped over the three-dimensional space between the sputter target and substrate using a triple Langmuir probe. Plasma density is shown to decrease by greater than an order of magnitude between pulses. The effects of pulse duration, current density, pulse shape, switching frequency, and target material on the discharge are explored and discussed.

Surface Science
Room: M - Session SS1-MoM

Vibrational Spectroscopy and Surface Reactions
Moderator: Y. Chabal, University of Texas, Dallas

8:20am **SS1-MoM1 Reaction of Phenylenediamines on Ge(100)-2x1: The Effects of Functional Group Spacing on Reactivity**, ***J.S. Kachian***, *K.H. Squires, S.F. Bent*, Stanford University

While silicon is the current material of choice in the electronics industry, next-generation device requirements make the largely unexplored surface chemistry on germanium, a Group IV homolog with promising electrical properties, an interesting area of study. Multifunctional adsorbates are of particular interest, since they inherently offer a greater degree of tailorability and the potential for subsequent reaction. The adsorption of the o-, m- and p- structural isomers of phenylenediamine on Ge(100)-2x1 at room temperature was investigated to gain a fundamental understanding of how surface bonding of these molecules is affected by the distance between two NH_2 groups attached to a rigid benzene ring. Vibrational spectra of the adsorption products of these three molecules, obtained via multiple internal reflection Fourier transform infrared (MIR-FTIR) spectroscopy in ultrahigh vacuum (UHV), show that all three isomers adsorb via N-H dissociation. The corresponding X-ray Photoelectron Spectroscopy (XPS) results support the MIR-FTIR data and further reveal the bonding configurations of the N-H dissociated adducts at the surface: While there is evidence of both singly and dually N-H dissociated adducts for the ortho isomer, N-H dissociation of only one amino group is observed for the para isomer, while N-H dissociation of both amino groups is observed for the meta adducts. Dative bonding was not observed for reaction of any of the phenylenediamine isomers with the Ge(100)-2x1 surface. The difference in reactivity between isomers likely results from how closely the spacing between NH_2 groups on the benzene ring matches the distance between adjacent surface dimers. The distance is in closest agreement for the meta isomer, which adsorbs exclusively via dual N-H dissociation, and is most mismatched for the para isomer, which adsorbs only via single N-H dissociation. Adsorption of the ortho isomer, which represents an intermediate case geometrically, leads to a mixture of singly and dually N-H dissociated adducts. DFT calculations support the experimental results. The results will be compared to those obtained for reaction of aniline, the monofunctional analog to the phenylenediamine isomers, on Ge(100)-2x1.

8:40am **SS1-MoM2 Electronic and Steric Effects in the Reactions of Isocyanates and Isothiocyanates at the Ge(100)-2x1 Surface**, ***P.W. Loscutoff***, *K.T. Wong, S.F. Bent*, Stanford University

Organic functionalization of semiconductor surfaces has seen increased interest in recent years, due to the ever-decreasing feature sizes of microelectronics, and the advance of organic electronics. Advances in both of these fields require precise interface control at atomic dimensions, and modification of surfaces with organic molecules provides the flexibility necessary for use in a broad spectrum of applications. In this study, we examine the surface products formed by the reactions of various isocyanates and isothiocyanates with the Ge(100)-2x1 surface. Although these two moieties differ only by substitution of an oxygen atom with a sulfur atom, they display markedly different reactivity at the reconstructed germanium surface. Using a combination of infrared spectroscopy, x-ray photoelectron spectroscopy and density functional theory, we examine the reactions of phenyl, *tert*-butyl, and ethyl isocyanate and the corresponding isothiocyanates. Both phenyl isocyanate and phenyl isothiocyanate form multiple adsorption products at the surface. The isocyanate reacts with a Ge surface dimer to form a [2+2] cycloaddition product across the C=N bond to produce a surface-bound carbonyl in addition to other products. In contrast, phenyl isothiocyanate reacts across the C=S bond to form a [2+2] cycloaddition product, in addition to reaction across the C=N bond. When the *tert*-butyl group is substituted for the phenyl ring, the reactivity changes such that dative-bonded products with an intact, surface-bound isocyanate or isothiocyanate group are observed. Upon reaction of ethyl isocyanate and ethyl isothiocyanate at the Ge(100)-2x1 surface, yet another product distribution is observed, which lacks dative-bonded products but demonstrates time-dependence. The wide array of products observed for this set of isocyanate and isothiocyanate molecules demonstrates the influence of the molecular chain on the surface reactivity of these groups, and displays a versatility that could prove useful for tuning reactivity to achieve a desired surface product.

9:00am **SS1-MoM3 Surface Transamination Reactions for Thin Film Deposition on NH$_x$-Precovered Silicon***, **A.V. Teplyakov***, University of Delaware **INVITED**

The termination of semiconductor surfaces plays a major role in surface reactivity and in our ability to create a well defined and sharp interface between a semiconductor and a thin film, often required for practical applications. Although hydrogen termination of group IV semiconductors is often a good starting point for deposition chemistry, the reactivity of hydrogen terminated surfaces is often limited. Here we selectively produce a specific NH$_x$ termination of Si(100) surface by exposing it to ammonia and briefly annealing at a predetermined temperature. The reactivity of silicon surfaces prepared in such a way is examined by reacting them with a common organometallic precursor for thin diffusion barrier film growth, tetrakis(dimethylamido)titanium, TDMAT. Experimental observations suggest the occurrence of a surface transamination reaction, where an approaching TDMAT molecule reacts with a surface NH$_X$ site, eliminating dimethylamine and attaching Ti to the surface N atom. Vibrational spectroscopy holds the key to determining this reactivity and surface reaction pathways. Together with temperature programmed desorption and computational DFT investigations, these studies expand the generality of transamination processes to other amines on Si(100). The role of steric and electronic factors is evaluated for improving proposed deposition schemes.

9:40am **SS1-MoM5 Si ALE using Molecular Disilane on Si(100)-(2x1)***, **I.S. Chopra**, J.-F. Veyan, M.P. Nadesalingam, N. Dao, O. Seitz, W.P. Kirk,* The University of Texas at Dallas*, J. Randall,* Zyvex Labs*, M. Huang, K. Cho, R.M. Wallace, Y. Chabal*, The University of Texas at Dallas

Atomic layer epitaxy (ALE) is a critical step in trying to achieve Atomically Precise Manufacturing (APM) of new devices such as quantum dots, qubits, NEMS oscillators and biomedical devices. Here we report the ALE of Si using molecular disilane on (2x1)-Si(100) surface. The surfaces have been characterized using Fourier transform infrared spectroscopy (FTIR), angle resolved x-ray photoelectron spectroscopy (ARXPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS).

IR absorption measurements have been performed in transmission mode (70^o incidence). Clean Si(100)x(2x1) samples are prepared by controlled thermal desorption of chemically oxidized Si wafers. On clean (2x1) – Si(100) surfaces, saturation doses of the order of 10L are observed, which is considerably lower than data reported earlier (3000L)[1.] At saturation coverage absorption bands in the ~2100 cm^{-1} range (and also ~950 and 650 cm^{-1}) indicate that monohydrides (SiH), dihydrides (SiH$_2$) and trihydrides are formed, consistent with shifts of the Si2p core level using angle resolved X-ray photoelectron spectroscopy. The relative intensities of these bands have been studied as a function of exposure and substrate temperature, and present differences from earlier room temperature measurements.[2] The observation of trihydrides indicates that one product from disilane decomposition is the silyl group, although its concentration depends on exposure and temperature. The thermal stability of these resulting surfaces has been examined with infrared absorption, temperature-programmed desorption (TPD) and LEED. We have also examined the effects of He ion surface de-passivation.[3]

To gain a fundamental understanding on surface reaction mechanisms, we have performed a density functional theory (DFT) study on the reactions of monohydrides (SiH), dihydrides (SiH2), trihydrides and disilane on both clean and hydrogen passivated Si(100)-(2x1) surfaces. The calculated atomic configurations, electronic structures, and vibration frequencies are compared with the experimental data.

References

1 Yoshiyuki Suda, Naoyuki Hosoya and Kazushi Miki, Appl. Surf. Sci. 216, 424-430 (2003).

2 Masanori Shinohara, Michio Niwano, Yoichiro Neo and Kuniyoshi Yokoo, Thin. Solid Films 309, 16-20 (2000).

3 This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

10:00am **SS1-MoM6 Adsorption Studies of Molecular Disilane on p-type Ge(100) at Room Temperature***, **M.P. Nadesalingam**, N. Dao, I.S. Chopra, J.-F. Veyan, W.P. Kirk,* University of Texas at Dallas*, J. Randall,* Zyvex Labs*, Y. Chabal, R.M. Wallace*, University of Texas at Dallas

ALE (Atomic Layer Epitaxy) is a layer by layer epitaxial thin film growth technique of interest for fabrication of SiGe high speed devices[1] as well as enabling atomically precise manufacturing (APM) of nanometer scale features. We report on a precision gas dosing technique for Si ALE on Ge(100) p-type using molecular disilane.

The adsorption of molecular disilane on Ge(100) was studied using X-ray photoelectron spectroscopy (XPS), low energy electron diffraction (LEED) and quadrupole mass spectrometry (QMS) and Fourier transform infrared spectroscopy (FTIR). LEED analysis shows that the Ge surface periodicity results in a weak 2x1 pattern upon exposure to molecular disilane. The molecular disilane was delivered to the Ge(100) substrate using micro-capillary array molecular beam doser with an equivalent dose of ~1.2 L, which is a considerably smaller value compared to that reported from previous techniques.[2] Based on the XPS data, the Si coverage on Ge is nearly half a monolayer.[3] The sticking coefficient of molecular disilane on Ge (100) is estimated to be 0.48 with disilane adsorption on Ge(100) that is governed by dissociating Si$_2$H$_6$ into two silyl(-SiH$_3$) groups. IR absorption measurements have been performed in transmission mode (70^o incidence) to analyze the adsorption mechanisms as a function of temperature and coverage.[4]

References

1. Y. Suda, H. Koyama, Appl. Phys. Lett. **79**, 2273 (2003).

2. Yoshiyuki Suda, Yasuhiro Misato, Daiju Shiratori, J. of Cryst. Growth **237-239**, 1404 (2002).

3. D. S. Lin, T. Miller and T. C. Chiang, Phys. Rev. **B 47**, 6543 (1992).

4. This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

10:40am **SS1-MoM8 High-stability Molecular Interfaces to TiO$_2$ Surfaces***, **R. Franking**, H. Kim, E.C. Landis,* University of Wisconsin, Madison*, S.A. Chambers,* Pacific Northwest National Laboratory*, R.J. Hamers*, University of Wisconsin, Madison

The integration of molecular systems with TiO2 is of interest in a wide range of emerging applications; however, most methods currently used are not stable under in aqueous media, especially at elevated temperatures or extremes of pH. We demonstrate that well-defined molecular layers can be covalently bound to the surface of nanocrystalline and single-crystal anatase TiO2 by photochemically grafting organic molecules bearing a terminal vinyl group. Stability tests on nanocrystalline films show the layers have excellent stability in aqueous environments with a wide range of pH for time scales approaching 2 months, and that grafting occurs through the thickness of 10 micron thick porous films. XPS, FTIR, and wavelength-dependent excitation experiments have been performed to help identify the reaction pathway. New methods are being developed using the highly stable chemistry to create highly flexible, modular interfaces with the oxide.

11:00am **SS1-MoM9 HREELS Study on the Doping of ZnO by H and Cu Atoms***, H. Qiu, **Y. Wang**, Ch. Wöll*, Ruhr-University Bochum, Germany

Zinc oxide exhibits a number of extraordinary properties and is one of the most technologically important metal oxides [1]. Presently, there is great interest in the doping of ZnO by foreign atoms due to its effects on changing the electrical, optical and catalytic properties of ZnO. In this contribution, the interaction of hydrogen and Copper atoms with ZnO(000-1) was studied by high resolution electron energy loss spectroscopy (HREELS) which recently has been successfully applied to perfect and defective metal oxide surfaces [2].

Exposing the fully hydroxylated ZnO(000-1) surface to atomic hydrogen leads to a significant broadening of the quasi-elastic peak in HREELS, which corresponds to the existence of free charge carriers at ZnO surface region [3]. These free charge carriers result from the thermal excitation of electrons at the donor level into the conduction band. The shallow donor states are created via diffusion of H atoms into the bulk. The analysis of the temperature dependence yields a shallow donor ionization energy of 25 ± 5 meV [4].

Cu deposition on O-ZnO leads to the formation of well-defined islands with the Cu(111) facets. For the small clusters the partial oxidation of Cu0 into Cu+ was clearly identified by the characteristic C-O stretching frequencies. Upon heating the Cu atoms undergo, instead of desorption, diffusion into the bulk. The doping of ZnO by Cu leads also to the formation of shallow donor states, in which the electrons can be thermally excited into the conduction band and, as a result, giving rise to the plasmon-induced broadening of the quasielastic peak in HREELS. From the observed temperature dependence, the donor level ionization energy was determined. This unexpected doping effect of ZnO by Cu has important consequences for its chemical activity, as confirmed by the detailed studies on CO2 adsorption.

[1] Ch. Wöll, Prog. Surf. Sci. 82 (2007) 55.

[2] Y. Wang, Z. Phys. Chem. 222 (2008) 927.

[3] Y. Wang, B. Meyer, X. Yin, M. Kunat, D. Langenberg, F. Traeger, A. Birkner, Ch. Wöll, Phys. Rev. Lett. 95 (2005) 266104.

[4] H. Qiu, B. Meyer, Y. Wang, Ch. Wöll, Phys. Rev. Lett. 101 (2008) 236401.

11:20am **SS1-MoM10 Reactions of NO$_2$ with BaO and Ba(OH)$_2$ on Pt(111)**, ***K. Mudiyanselage***, Pacific Northwest National Laboratory, *C.W. Yi,* Sungshin Women's University, Korea, *J. Szanyi*, Pacific Northwest National Laboratory

Reactions of NO$_2$ (in the pressure range of 1.0×10^{-9} - 1.0×10^{-4} Torr) with BaO(> 20 MLE), amorphous-Ba(OH)$_2$ and crystalline-Ba(OH)$_2$ supported on Pt(111) were studied using infrared reflection absorption spectroscopy (IRAS), temperature programmed desorption (TPD) and X-ray photoelectron spectroscopy (XPS). The amorphous and crystalline Ba(OH)$_2$ layers were prepared by adsorbing H$_2$O on BaO(> 20 MLE)/Pt(111) at 300 and 425 K, respectively. The amorphous-Ba(OH)$_2$ layer partially converts to Ba(NO$_x$)$_2$ (nitrites and nitrates) following exposure to elevated NO$_2$ pressure (~1.0×10^{-4} Torr) at 300 K. The exposure of the crystalline-Ba(OH)$_2$/Pt(111) system to NO$_2$ at 425 K leads to the desorption of H$_2$O and the complete conversion of the crystalline-Ba(OH)$_2$ layer to Ba(NO$_x$)$_2$, which consists of mainly crystalline nitrates and a small amount of nitrites. Adsorption of NO$_2$ on BaO(> 20 MLE)/Pt(111) at 425 K also forms crystalline nitrates. The amounts of NO$_x$ uptaken by BaO(> 20 MLE)/Pt(111) and crystalline-Ba(OH)$_2$/Pt(111) systems at 425 K are very similar as determined by the NO TPD peak areas.

11:40am **SS1-MoM11 In-situ Spectroscopy Studies of Surface Species on Pd Surfaces during CO Oxidation**, ***M.S. Chen***, *X. Wang, H.L. Wan*, Xiamen University, China

Previous we had found that CO oxidation on Pd-group metals at temperatures between 450 and 600 K and pressures between 1 and 300 Torr increases markedly with an increase in the O$_2$/CO ratio above 0.5.[Surf. Sci. 2007,601, 5326.] The catalytic surfaces, formed at discrete O$_2$/CO ratios > 0.5, exhibit rates 2 to 3 orders of magnitude greater than those rates observed for stoichiometric reaction conditions and similar reactant pressures or previously in ultrahigh vacuum studies at any reactant conditions and extrapolate to the collision limit of CO in the absence of mass transfer limitations. Here we used HREELS to address the relative activities of surface CO and oxygen species. The surface oxygen species can be removed by CO at room temperature and low pressure, 10^{-8} Torr. While a much higher oxygen pressure or above room temperature is required to remove surface adsorbed CO species. Furthermore, *in-situ* RAIRS and Raman spectroscopy were used to characterize this highly active surface formed at higher O$_2$/CO ratios on Pd.

Keywords: CO oxidation, Pt-group metal, Oxygen covered surface

Surface Science
Room: N - Session SS2-MoM

TiO2 Surfaces and Interfaces
Moderator: D.A. Chen, University of South Carolina

8:20am **SS2-MoM1 Surface Structures of TiO$_x$ Thin Films on Au (111)**, ***C. Wu***, *M.R. Castell*, Oxford University, UK

Well-ordered ultrathin titanium oxide layers were grown on reconstructed Au (111) surfaces by Ti evaporation at room temperature and post-deposition oxidation at a pressure of 10-6 Pa O2 and a temperature of around 600 °C. Depending on the amount of Ti deposited, three different structures were observed. The structures were characterized by scanning tunnelling microscopy (STM), X-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES).

With Ti coverage below one monolayer (ML), an epitaxial oxide honeycomb structure is created. The herringbone reconstruction of the Au (111) substrate is lifted underneath the titanium oxide monolayer. STM reveals that the contrast between the honeycomb monolayer and the gold reconstruction is influenced by both tip termination and imaging bias. The measured periodicity and crystallographic alignment of the honeycomb structure indicates a (2×2) reconstruction on Au (111). XPS and AES data show the deposited titanium is fully oxidised to TiO2. Increasing the Ti dose up to 2 MLs gives rise to a pinwheel structure that coexists with the honeycomb on the surface. The spokes of the pinwheels are parallel to the three close-packed directions of the honeycomb structure. Triangular islands start to grow and coalesce with higher Ti coverage. It is difficult to resolve the structure on the islands, but after 1.5 hours annealing of the thicker films, a row-like structure can be observed with a periodicity of 0.95 nm across the rows. XPS and AES indicate the presence of the Ti2+ oxidation state.

8:40am **SS2-MoM2 Geometric Structure of the TiO$_2$(011) (2x1) Surface by Low Energy Electron Diffraction (LEED)**, ***S.E. Chamberlin***, *H.C. Poon, D.K. Saldin, C.J. Hirschmugl*, University of Wisconsin - Milwaukee

The surface of TiO$_2$ has been extensively studied to explore its potential for many applications, including the harvesting of solar light and the photocatalysis of water [1-3]. The majority of studies have focused on the thermodynamically most stable rutile (110) face [4], however, other faces are almost as important. For example, the rutile (011) face may have enhanced activity towards water dissociation [5], but is less studied. Crucial to understanding the mechanisms by which these processes occur is determining the atomic structure and chemistry of the surface.

The (011) surface of TiO$_2$ is known to exhibit a (2x1) reconstruction [6] and several models of the surface have been proposed [6-9]. The present work extends quantitative low energy electron diffraction (LEED) to reconstructed oxide surfaces in order to determine which, if any, of these models are supported by LEED-IV. I-V curves, with a total energy range of ~2200 eV, were extracted for 20 beams using a novel, low-current, delay-line-detector LEED (DLD-LEED) system to minimize effects due to charging and electron beam damage. Structural refinement from the LEED-IV analysis confirms the Brookite model [8] found by surface x-ray diffraction, with agreements in atomic displacements to within 0.04 Å perpendicular to the surface and 0.12 Å parallel to the surface. The resulting Pendry R-factor is 0.29 which definitively excludes the other proposed models that give significantly higher R factors.

---

[1] A. Fujishima and K. Honda, Nature (London) **238**, 37 (1972)

[2] M. Gratzel, Nature **414**, 338 (2001)

[3] T.L. Thompson and J.T. Yates, Chem. Rev. **106**, 4428 (2006)

[4] M. Ramamoorthy, D. Vanderbilt, and R.D. King-Smith, Phys. Rev. B **49**, 16721 (1994)

[5] J.W. Lowekamp, G.S. Rohrer, P.A.M. Hotsenpilller, J.D. Bolt, and W.E. Farneth, J. Phys. Chem. B **102**, 7323 (1998)

[6] T. J. Beck *et al.*, Phys. Rev. Lett. **93**, 036104 (2004)

[7] T. Kubo, H. Orita, and H. Nozoye, J. Am. Chem. Soc. **129**, 10474 (2007)

[8] X. Torrelles *et al.*, Phys. Rev. Lett. **101**, 185501 (2008)

[9] X.Q. Gong *et al.*, Surf. Sci., **603**, 138 (2009)

9:00am **SS2-MoM3 Metal Oxide Surfaces: Defects, Dopants, and Reactivity**, ***U. Diebold***, Tulane University **INVITED**

Metal oxides are versatile materials and are used in a wide variety of technical fields. In many applications, surface properties play a critical role in device functioning. Our group is investigating the atomic-scale properties of metal oxide surfaces with Scanning Tunneling Microscopy (STM) and area-averaging surface spectroscopies. DFT calculations, conducted in collaboration with theoretical groups, are instrumental in data analysis and interpretation.

In the talk we report recent results on metal oxide materials that have industrial relevance but are rarely studied with surface science techniques. We find that on a TiO$_2$ anatase (101) surface standard preparation procedures lead to *sub*surface rather than surface oxygen vacancies [1]. Adsorbed water shows an interesting short-range ordering that is governed by substrate-mediated repulsive/attractive interactions [2]. The surface structure of epitaxial films of Sn-doped In$_2$O$_3$ (ITO) is discussed [3].

[1] Y. He et al., Phys. Rev. Lett. 102, 106105 (2009).

[2] Y. He et al., Nature Mater. in press (2009).

[3] E. H. Morales et al., New Journal of Physics, 10 (2008) 125030

9:40am **SS2-MoM5 Controlled Manipulation of Oxygen Vacancies on TiO_2(110)-1x1 Using LT-STM**, ***D. Acharya***, *P.W. Sutter*, Brookhaven National Laboratory

Titanium dioxide (TiO2) – widely used in, photocatalysis, heterogeneous catalysis, gas sensors, and solar cells – has become the prototype material for studying the chemical reactivity of metal oxide surfaces. Oxygen vacancies are among the primary chemically active defects on this surface, as well as on other reducible transition metal oxides. We report the controlled manipulation of individual O-vacancies (Ov) on reduced TiO2 (110)-1x1 in low temperature scanning tunneling microscopy. Using localized voltage pulses, the hopping of oxygen vacancies can be controlled precisely along the bridging oxygen rows. We apply this single-vacancy manipulation to study the interaction of closely spaced vacancies, and to establish the possibility of forming highly reactive double and triple Ov clusters. The occurrence of such defects with exposed low-coordinated Ti atoms has implications on the reactivity of TiO2(110) and of similar metal-oxide surfaces.

10:00am **SS2-MoM6 Oxygen Reactivity on Reduced TiO_2(110)**, ***N.G. Petrik***, *G.A. Kimmel*, 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, the thermal and non-thermal (photon- and electron-stimulated) reactions of molecular oxygen are studied versus oxygen coverage on reduced TiO_2(110). At low temperatures, two O_2 can chemisorb per oxygen vacancy (V_O).[1] Hydroxylation of the vacancies (via dissociative water adsorption) does not affect the amount of chemisorbed O_2. Most of the chemisorbed molecules do not desorb upon annealing to 700 K, but react. The thermal reactions of the chemisorbed O_2 depend strongly on the oxygen coverage. When 1 O_2 is adsorbed in an oxygen vacancy, the molecule dissociates upon annealing above ~200 K, healing the vacancy and depositing an oxygen adatom on the Ti row. At an oxygen coverage of 2 O_2 per oxygen vacancy, the oxygen converts to another species (perhaps tetraoxygen or ozonide) in temperature range of $200\ K < T < 400\ K$. This species subsequently decomposes at higher temperatures. The photon- (and electron-) stimulated desorption of chemisorbed oxygen are also very sensitive to the oxygen coverage. The results demonstrate that the reactivity of TiO_2(110) with O_2 is primarily controlled by the amount of electron-donating surface species on the surface (V_O's and/or hydroxyls).[2]

[1] G.A. Kimmel and N.G. Petrik, Phys. Rev. Lett. 100, 196102 (2008).

[2] N.G. Petrik, Z. Zhang, Y. Du, Z. Dohnalek, I. Lyubinetsky, G.A. Kimmel, JCP submitted

10:40am **SS2-MoM8 Oxygen Interactions with Hydroxylated TiO_2(110) Surfaces**, *Y. Du, A. Deskins, Z. Zhang, N.G. Petrik, G.A. Kimmel, Z. Dohnalek, M. Dupuis*, ***I. Lyubinetsky***, Pacific Northwest National Laboratory

Reactions leading from O_2 to H_2O on catalytically active surfaces often involve intricate mechanisms with a number of possible surface-bond intermediates, such as OH, HO_2, or H_2O_2. Such reactions on surfaces are challenging to explore with ensemble-average techniques because of the extremely small number of participating molecules and the difficulty in resolving intermediates spectroscopically.

In this work, the reaction of O_2 with both partially and fully hydroxylated TiO_2(110) surface was directly followed by STM. The consecutive steps of both primary and secondary site-specific reactions have been tracked by comparing the atomically resolved STM images of same surface area before and after O_2 exposure. As a result, we have directly imaged two chemical intermediates, terminal OH and OOH, which have been proposed to play key roles in the interconversion of oxygen and water. By combining the site-specific STM and ensemble-averaging TPD/ESD studies, we also find that H_2O can participate in the reaction process in multiple ways – as a reactant, product, and catalyst. Specifically, water mediates the diffusion of surface species that would otherwise be stationary, and thus brings reactants together, catalyzing the reactions with O_2. As a result, most of the OH_b's can be removed via reaction with O_2 such that a fully hydroxylated surface can be converted to a nearly stoichiometric surface.

11:00am **SS2-MoM9 The Photochemistry of Trifluoroacetone on TiO_2(110)**, ***R.T. Zehr***, *M.A. Henderson*, Pacific Northwest National Laboratory

The ultraviolet (UV) photon induced photodecomposition of 1,1,1-trifluoroacetone (TFA) adsorbed on the rutile TiO2(110) surface has been investigated with photon stimulated desorption (PSD) and thermal programmed desorption (TPD). TFA adsorbed on the reduced surface (8% oxygen vacancies) showed a molecular desorption peak at 260 K that shifts to 220 K with increasing TFA coverage, indicative of inter-adsorbate repulsion in the adsorbed layer. Adsorption of TFA on a reduced TiO2 surface pre-exposed to 20 L O2 leads to the formation of a TFA peak at 350 K accounting for 2/3rd ML coverage. A second peak at 250 K (1/3rd ML) completes the monolayer. Irradiation of the TFA covered oxidized surface by UV light at 90 K reduces the intensity of the 350 K TPD peak, with the 250 K state unaffected. Post-irradiation TPD shows evidence of the formation of small amounts of acetate (evolving as ketene at 650 K) as a surface bound decomposition product. UV irradiation of TFA causes the near complete photodecomposition of the photoactive species, leading to PSD of CH3, CF3, and CO during irradiation. This result is in contrast to the photochemical behavior of acetone, butanone and acetaldehyde on TiO2(110), where the gas phase ejection of only one of the two carbonyl substituent groups is observed and a stoichiometric amount of carboxylate is left on the surface. We conclude that fluorination alters the electronic structure of adsorbed carbonyls on TiO2(110) in such a way as to promote complete fragmentation of the adsorbed carbonyl complex.

(This work was supported by the DOE Office of Basic Energy Sciences, Division of Chemical Sciences and performed in the Environmental Molecular Sciences Laboratory at PNNL.)

11:20am **SS2-MoM10 TiO_2 with Subsurface Metallic Nanoclusters for Stimulating Photochemistry**, *F. Womack, F. Wang, Z. Zhang, P. Sprunger,* ***R.L. Kurtz***, Louisiana State University

Metallic nanoclusters can be buried within nanometers of the surface of TiO_2 and can enhance photoabsorption to produce hot electron-hole pairs for surface chemistry. When Ag is grown on TiO_2(110), STM shows that it forms ~ 5nm clusters, and HREELS shows a plasmon resonance at 3.7 eV. AFM shows that these clusters remain after coating with a thin layer of titania and conducting probe AFM shows that the conductivity in the vicinity of the clusters is enhanced consistent with their metallic nature and increased defect densities in the oxide. HREELS shows that the plasmon resonance of the nanocluster is red-shifted and broadened to 1.5-2 eV when encapsulated in titania and these findings are supported by optical measurements. The nanoclusters induce defects within the surrounding titania and the role that Ti^{3+} defects, O-vacancies, and Ti-interstitials play in Ag/TiO_2 interactions as probed with synchrotron-based photoemission will be discussed. Electrochemical measurements have been conducted to test photochemical performance in electrolyte, and subsequent surface analysis provides information on the changes induced in morphology, defect densities, and oxidation states.

We acknowledge the support of NSF through CHE-0615606.

11:40am **SS2-MoM11 Switching of Sulfur Lattice Sites in S-doped TiO_2(110) Under Controlled Annealing Environments**, ***N. Athavan***, Portland State University, *V. Shutthanandan, P. Nachimuthu, S. Thevuthasan*, Pacific Northwest National Laboratory

TiO_2 is one of the most heavily studied materials for photocatalytic water splitting even though it has a poor overlap of its optical absorption spectrum with the solar spectrum and high e^-/h^+ pair recombination rate. Band gap reduction is one approach to enhance visible light absorption in TiO_2. Anion (N, C and S) doping causes a red shift of the absorption edge into the visible region and visible-light-induced photochemistry has been observed on these materials. Recently, we have investigated S doped TiO_2(110) rutile by ion implantation as a function of substrate temperatures and dopant concentrations. Subsequently high-temperature annealing was carried out on selected samples to heal the implantation damage as well as to understand the location and mobility of the dopants in the rutile lattice. Following implantation and annealing, the samples were characterized using several surface and bulk sensitive techniques such as x-ray photoelectron spectroscopy (XPS), Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA) and proton induced x-ray emission (PIXE) in both random and channeling directions. Depth profile of S implanted TiO_2 was obtained using XPS. PIXE was used to locate the lattice sites of S while NRA and RBS were used to measure the lattice sites of oxygen and titanium atoms, respectively. PIXE measurements along the channeling and random geometries clearly demonstrate the substitution of sulfur for oxygen in TiO_2 lattice under certain implantation conditions. Angular scans obtained around <110> were used to investigate the lattice site locations of sulfur at different annealing conditions. When the implanted sample is further annealed at 700^{o}C for 1 hour at 100 Torr of oxygen, the sulfur atoms moved from the substitutional sites to interstitial sites. Subsequent annealing in vacuum (1 x10^{-5} Torr) at 800^{o}C for 1 hour showed that the displaced sulfur atoms reoccupied the substitutional sites. Additional vacuum annealing at 900^{o}C is not only retained the S atoms at the oxygen lattice sites but also improved the overall crystalline quality of the implanted region.

This work is supported by grants from DOE BES Division of Chemical Sciences and Office of Biological and Environmental Research

Thin Film
Room: B3 - Session TF1-MoM

Thin Films: Growth and Characterization I
Moderator: S. Gupta, University of Alabama

8:40am **TF1-MoM2 Photoluminescence Properties of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ Thin Phosphor Films Grown by Pulsed Laser Deposition**, ***O.M. Ntwaeaborwa***, *P.D. Nsimama, H.C. Swart*, University of the Free State, South Africa

Thin films of $SrAl_2O_4:Eu^{2+},Dy^{3+}$ phosphor were grown on silicon substrates using a 248 nm KrF pulsed laser to evaluate the effects of different processing parameters on photoluminescence properties of the phosphor. The processing parameters which were varied during the films growth include temperature, pressure, and the number of pulses. X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) were used to examine the structure, particle morphology and surface topography of the films. The chemical composition and thicknesses of the films were determined by Rutherford backscattering spectroscopy (RBS). Photoluminescence spectra of the films recorded by the Cary Eclipse spectrophotometer were characterized by major green phosphorescent emission with a maximum at ~520 nm and minor red emission with a maximum at 630 nm. The green and red photoluminescence at 520 and 630 nm are associated with the $4f^65d \rightarrow 4f^7(^8S_{7/2})$ and $^5D_0$-$^7F_2$ transitions of Eu^{2+} and residual Eu^{3+} ions respectively. The effects of processing parameters on the PL intensity and the possible mechanism of the green phosphorescence were discussed.

9:00am **TF1-MoM3 Multifunctional Double Perovskite Thin Films and Heterostructures**, ***A. Gupta***, The University of Alabama **INVITED**

A double perovskite is a perovskite with the general formula of $A_2BB'O_6$, where A is a divalent alkaline earth cation and B and B' are transition-metal ions. Depending on the relative size and oxidation state, the B and B' ions can be crystallographically completely ordered, making up a rocksalt-type lattice. La_2NiMnO_6 is an ordered double perovskite that is a ferromagnetic semiconductor with a T_{CM} of 280 K. Recent studies of La_2NiMnO_6 in the bulk have revealed large magnetic-field induced changes in the resistivity and dielectric properties at temperatures as high as 280 K [1,2]. This is a much higher temperature than previously observed for such a coupling between the magnetic, electric, and dielectric properties in a ferromagnetic semiconductor. Substitution at the *A* site can also lead to multiferroic behavior in the double perovskites. Azuma *et al.* have succeeded in synthesizing the 'designed' compound Bi_2NiMnO_6 in the bulk under high pressure and established its multiferroic properties, with ferroelectric and ferromagnetic transition temperatures of 485 K and 140 K, respectively [3]. We have synthesized epitaxial thin films of La_2NiMnO_6 [4], Bi_2NiMnO_6 [5], and their heterostructures using the pulsed laser deposition (PLD) technique. A related ferromagnetic semiconductor, La_2CoMnO_6, has also been epitaxially stabilized [6]. High quality epitaxial films of these double perovskites are grown on lattice-matched substrates such as $SrTiO_3$, $NdGaO_3$ and $LaAlO_3$. We have structurally characterized the double perovskite films using a variety of techniques. Additionally, the magnetic, electrical and magnetodielectric properties of the thin films and heterostructures have been studied in detail.

[1] N. S. Rogardo, J. Li, A. W. Sleight, and M. A. Subramanian, Adv. Mater. **17**, 2225 (2005).

[2] H. Das, U. V. Waghmare, T. Saha-Dasgupta, and D. D. Sarma, Phys. Rev. Lett. **100**, 186402 (2008).

[3] M. Azuma, K. Tanaka, T. Saito, S. Ishiwata, Y. Shimakawa, and M. Takano, J. Am. Chem. Soc. **127**, 8889 (2005).

[4] H. Guo, J. Burgess, S. Street, A. Gupta, T. G. Calvarese, and M. A. Subramanian, Appl. Phys. Lett. **89**, 022509 (2006).

[5] P. Padhan, P. LeClair, A. Gupta, and G. Srinivasan, J. Phys.: Condens. Matter **20**, 355003 (2008).

[6] H. Z. Guo, A. Gupta, T. G. Calvarese, and M. A. Subramanian, Appl. Phys. Lett. **89**, 262503 (2006).

9:40am **TF1-MoM5 Influence of Nanostructure on Charge Transport in RuO_2 Thin Films**, ***M.M. Steeves***, *R.J. Lad*, University of Maine

Ruthenium dioxide exhibits metallic electrical conductivity, and may have both electron and hole contributions to its charge transport. In this study, polycrystalline thin films of RuO_2 were grown on fused quartz substrates by RF reactive magnetron sputtering, and a parametric study was carried out to probe the influence of film nanostructure on the four-point Van der Pauw resistivity and Hall coefficient. The films were grown via reactive RF magnetron sputtering of a Ru target in an Ar/O_2 plasma using a range of deposition rates and with substrate temperatures ranging from 20-500°C. A wide variety of nanostructures and film textures were obtained as determined by high resolution x-ray diffraction for film thicknesses ranging from 40-180 nm as measured by x-ray reflectivity and profilometry. The films exhibited strains of the order of 0.5% and average crystallite sizes ranging from 20-70 nm. Room temperature resistivities varied between 200-400 $\mu\Omega$ cm and showed a relatively weak dependence on temperature. Hall coefficients ranged from +200 to -200 $x10^{-5}$ cm^3/C as a function of temperature, depending on exact nanostructure as well as the heating environment. The observation of both positive and negative Hall coefficients for different RuO_2 films is in contrast to the reported single crystal value of -11 $x10^{-5}$ cm^3/C for which electrons are the majority carrier. Correlations between nanostructure and transport properties are given in terms of grain size, strain, film defects, and mobility of the majority carriers.

10:00am **TF1-MoM6 Electrical and Structural Properties of Ultrathin Polycrystalline and Epitaxial TiN Films Grown by Reactive dc Magnetron Sputtering**, *F. Magnus, A.S. Ingason, S. Olafsson,* ***J.T. Gudmundsson***, University of Iceland

Ultrathin TiN films were grown by reactive dc magnetron sputtering on amorphous SiO_2 substrates and single-crystalline MgO substrates at various growth temperatures. The resistance of the films was monitored in-situ during growth to determine the coalescence and continuity thicknesses. TiN films grown on SiO_2 at 600°C are polycrystalline and have nominal coalescence and continuity thicknesses of 8 Å and 19 Å, respectively. TiN films grow epitaxially on the MgO substrates at 600°C. The nominal coalescence thickness is 2 Å and the thickness where the film becomes continuous cannot be resolved from the coalescence thickness. X-ray reflection measurements indicate a significantly higher density and lower roughness of the epitaxial TiN films.

10:40am **TF1-MoM8 Cubic and Wurtzite $Sc_{1-x}Al_xN$ Solid Solutions Grown by Reactive Magnetron Sputter Epitaxy onto ScN (111) and AlN(0001) Seed Layers**, ***C. Höglund***, Linköping University, Sweden, *J. Bareño,* Argonne National Laboratory, *J. Birch, B. Alling,* Linköping University, Sweden, *Z. Czigány,* Hungarian Academy of Sciences, Hungary, *L. Hultman*, Linköping University, Sweden

Reactive magnetron sputter epitaxy was used to grow thin solid films of $Sc_{1-x}Al_xN$ ($0 \le x \le 1$) onto ScN(111) and AlN(0001) seed layers at substrate temperatures of 600ºC and 800°C, respectively. The films were analyzed by Rutherford backscattering spectroscopy (RBS), elastic recoil detection analysis (ERDA), x-ray diffraction (XRD) and transmission electron microscopy (TEM). RBS and ERDA showed that stoichiometric films were obtained in the entire composition range (molar fractions x = 0, 0.14, 0.29, 0.51, 0.73, 0.90, 1.0) using elemental Sc and Al targets and N_2 as the reactive gas. TEM and XRD show that rocksalt structure (c) $Sc_{1-x}Al_xN(111)$ solid solutions can be epitaxially grown onto the isostructural c-ScN(111) seed layers with AlN molar fractions up to x ~ 0.6 , whereafter the system phase separates into c- and wurtzite structure (w) $Sc_{1-x}Al_xN$. Upon phase separation, the w-domains are present in three different orientations relative to the seed layer, namely $Sc_{1-x}Al_xN(0001)$ || ScN(111) with $Sc_{1-x}Al_xN[-12-10]$ || ScN[1-10], $Sc_{1-x}Al_xN(10-11)$ || ScN(111) with $Sc_{1-x}Al_xN[-12-10]$ || ScN[1-10], and $Sc_{1-x}Al_xN(10-11)$ || ScN(113). When growth was performed onto w-AlN(0001) seed layers, epitaxial w-$Sc_{1-x}Al_xN(0001)$ with AlN molar fractions x in the range ~0.50 to 1.00 were obtained. For AlN molar fractions of 0.28 and less, the film formed an epitaxial c-$Sc_{1-x}Al_xN(111)$ phase with double position domains.

The lattice parameter for the c-$Sc_{1-x}Al_xN$ films closely followed the values predicted by first principles density functional theory calculations, only slightly deviating from Vegard's law. On the contrary, the lattice parameters of the w-$Sc_{1-x}Al_xN$ varied considerably less than predicted. Our calculated mixing enthalpies of c-, w-, and zinc blende $Sc_{0.50}Al_{0.50}N$ solid solutions predict that the alloy is metastable with respect to phase separation for all temperatures below the melting points of AlN and ScN.

11:00am **TF1-MoM9 Process Control of Vanadium Oxide Thin Films Grown by Pulsed-dc Reactive Sputtering for Microbolometer Applications**, ***C. Venkatasubramanian***, *W.R. Drawl, S.S.N. Bharadwaja, M.W. Horn, S. Ashok*, The Pennsylvania State University

Low resistivity thin films of vanadium oxide with high temperature coefficient of resistance (TCR) are currently used as the imaging layer in uncooled infrared imaging. However, process control remains an issue because the films are formed under oxygen-starved conditions. In this paper, the influence of cathode current (target current) hysteresis on the properties of pulsed-dc reactive sputtered vanadium oxide thin films is investigated. VO_x thin films were sputter deposited from a vanadium metal target under different Ar/O ratios. The gas flow rates and oxygen partial pressures were varied systematically, and the corresponding changes in the cathode current were monitored. Increasing the gas flow rate from 10 sccm to 100 sccm caused the cathode current to decrease by ~25%, but on reversing the flow rate, the cathode current did not go back up along the same curve, instead exhibiting a hysteretic behavior. A similar trend was observed for the change in oxygen partial pressure between 0 and 20% as well. The width and position of the hysteresis curve depends on the relative values of the gas flow rates and the oxygen partial pressures. VO_x thin films deposited at various points along the hysteresis curve were evaluated using four-probe resistivity measurements over a wide temperature range. The room temperature resistivity of the films varied by more than six orders of magnitude and was found to have a progressive dependence on the cathode current. Structural characterizations such as X-ray diffraction and transmission electron microscopy studies indicated that the microstructure changes gradually from nano-crystallite to amorphous nature with the increase in total gas flow rate and/or oxygen partial pressure.

11:20am **TF1-MoM10 Compositional and Structural Evolution of Sputtered Ti-Al-N**, ***P.H. Mayrhofer***, *L. Chen, M. Moser,* Montanuniversitaet Leoben, Austria, *Y. Du*, Central South University, China

The compositional and structural evolution of Ti-Al-N thin films as a function of the total working gas pressure (p_T), the N_2-to-total pressure ratio (p_{N2}/p_T), the substrate-to-target distance (ST), the substrate position, the magnetron power current (I_m), the externally applied magnetic field, and the energy and the ion-to-metal flux ratio of the ion bombardment during reactive sputtering of a $Ti_{0.5}Al_{0.5}$ target is investigated in detail. Based on this variation we propose that the different poisoning state of the Ti and Al particles of the powder-metallurgically prepared $Ti_{0.5}Al_{0.5}$ target in addition to scattering and angular losses of the sputter flux cause a significant modification in the Al/Ti ratio of the deposited thin films ranging from ~1.05 to 2.15. The compositional variation induces a corresponding structural modification between single-phase cubic, mixed cubic-hexagonal and single-phase hexagonal. However, the maximum Al content for single-phase cubic $Ti_{1-x}Al_xN$ strongly depends on the deposition conditions and was obtained with $x = 0.66$, for the coating deposited at 500 °C, $p_T = 0.4$ Pa, ST = 85 mm, and $p_{N2}/p_T = 17\%$. Our results show, that in particular, the N_2-to-total pressure ratio in combination with the sputtering power density of the $Ti_{0.5}Al_{0.5}$ compound target has a pronounced effect on the Al/Ti ratio and the structure development of the coatings prepared.

Thin Film
Room: B4 - Session TF2-MoM

Metals and Nitrides (ALD/CVD)
Moderator: W.M.M. Kessels, Eindhoven University of Technology, the Netherlands

8:20am **TF2-MoM1 ALD of Metal Chalcogenide Thin Films**, ***M.A. Leskela***, *T. Hatanpaa, M.J. Heikkila, V.J. Pore, M.K. Ritala*, University of Helsinki, Finland **INVITED**

ALD of metal sulphide thin films has been known since the discovery of the technology in early 70s whereas ALD of metal selenide and telluride films has been limited because of a lack of precursors that would at the same time be safe and exhibit high reactivity as required in ALD. In this presentation we show that alkylsilanes of tellurium and selenium can be used as tellurium and selenium precursors in thermal ALD. Compounds with a general formula $(R_3Si)_2Te$ and $(R_3Si)_2Se$ react with various metal halides producing metal telluride and selenide thin films. Sb_2Te_3, GeTe and $Ge_2Sb_2Te_5$ films can be deposited by ALD at 90 °C using $(Et_3Si)_2Te$, $SbCl_3$ and $GeCl_2{\cdot}C_4H_8O_2$ as precursors. All three precursors exhibit a typical saturative ALD growth behaviour. The $Ge_2Sb_2Te_5$ films show excellent conformality on a high aspect-ratio trench structure. Many other selenide and telluride films can be deposited by ALD using alkylsilanes of tellurium and selenium as precursors. Those deposited in this work include ZnTe, Bi_2Te_3, ZnSe, Bi_2Se_3, In_2Se_3 and Cu_xSe_y. The growth temperature has in some cases been 400 ºC showing the thermal stability of these new Se and Te precursors. Growth rates of these binary chalcogenide films are typically between 0.5 and 1 Å/cycle. Other metal precursors than chlorides are also possible in the selenide and telluride depositions, as exemplified by the use of $GeBr_2$ and $Sb(OEt)_3$.

9:00am **TF2-MoM3 Molybdenum ALD and Mo/W Alloy Growth Using MoF_6, WF_6 and Si_2H_6 as the Reactants**, ***D. Seghete***, *A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Metal ALD using thermal chemistry is limited and based on combustion reactions (Ru, Pt), organic or H_2 reduction (Cu, Pd) or fluorosilane elimination (W). Molybdenum (Mo) is a refractory metal that has applications in alloys, catalysis and electronics. Mo ALD can be achieved with fluorosilane elimination chemistry using MoF_6 and Si_2H_6 as reactants. This process is similar to W ALD using WF_6 and Si_2H_6 as reactants. This study reports Mo ALD using a quartz crystal microbalance (QCM) to monitor the growth of the Mo ALD films and Mo/W alloy films in a hot wall viscous flow reactor.

QCM studies showed that Mo ALD is self-limiting for both MoF_6 and Si_2H_6 reactants. MoF_6 produces a large mass gain and Si_2H_6 produces a small mass loss. A mass gain of 535 ng/cm^2 per cycle was observed at 120°C when both reactant exposures were in saturation.

Although long MoF_6 residence times were observed on the surface, the Mo ALD growth per cycle was independent of purge time. The Mo film growth reached a linear regime after a short nucleation period of only 3-4 cycles on Al_2O_3 ALD surfaces. X-ray reflectivity (XRR) experiments confirmed linear Mo ALD growth versus number of cycles. A growth per cycle of 6.4 Å/cycle was measured at 120°C. The average density of the Mo films was 8.7 g/cm^3 and there was excellent agreement between the QCM and XRR experiments. The temperature dependence of the Mo ALD growth per cycle was investigated from 90 ºC to 150 ºC.

X-ray photoelectron spectroscopy confirmed negligible F concentrations in the Mo ALD films. However, higher Si concentrations were observed in the Mo ALD films compared with W ALD films. The variation of Si content in the Mo ALD films was examined versus growth temperature and dosing conditions. Various Mo/W alloys can be produced by alternating Mo ALD and W ALD. These alloys can eliminate crystalline grain growth that occurs in the pure metals. This reduction of crystalline grain growth relieves the internal mechanical stress that develops in pure W ALD films.

9:20am **TF2-MoM4 Vapor Deposition of Ruthenium Thin Films from an Amidinate Precursor**, *H. Wang, X. Wang, Y. Lin,* ***R.G. Gordon***, Harvard University, *R. Alvis,* FEI Company, *R.M. Ulfig*, Imago Scientific Instruments

Ruthenium thin films were deposited by pulsed chemical vapor deposition from bis(*N,N'*-di-*tert*-butylacetamidinato) ruthenium(II) dicarbonyl and O_2. Highly conductive, dense, conformal and pure thin Ru films can be deposited when oxygen exposure E_O approaches a certain low threshold (E_{max}). When $E_O > E_{max}$, the films peel off silica substrates, perhaps due to recombinative desorption of O_2 at the film/substrate interface. Ruthenium films grown on tungsten substrates show very strong adhesion, > 17 J m^{-2}, and no evidence for any oxidized interlayer between the Ru and the W. Thus the low oxygen exposure does not oxidize the tungsten substrate surface during Ru deposition. Analysis by an atomic probe microscope shows that the crystallites are nearly free of carbon impurity (<0.1at.%), while a low level of carbon(<0.5at.%) is segregated near the grain boundaries. The atom probe microscope also shows that a small amount of O impurity (0.3at.%) is distributed uniformly through the crystallites and the grain boundaries.

9:40am **TF2-MoM5 Thermal and Remote Plasma ALD of Ru from $CpRu(CO)_2Et$ and O_2**, ***N. Leick***, *R.O.F. Verkuijlen, E. Langereis,* Eindhoven University of Technology, The Netherlands, *S. Rushworth,* SAFC Hitech Limited Power Road, UK, *F. Roozeboom,* NXP Semiconductors Research, The Netherlands, *M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Ruthenium (Ru) is regarded as an electrode candidate on ultrahigh-*k* $SrTiO_3$ dielectric films for future high-density trench capacitors. To achieve conformal film growth, atomic layer deposition (ALD) of Ru is investigated. To this end, the use of an oxidizing reactant is desired to avoid electronic degradation of the interface properties of $SrTiO_3$ as found when using a NH_3 plasma for Ru ALD or when using thermal ALD TiN as electrode. Thermal ALD of Ru using O_2 gas, however, generally results in a pronounced nucleation delay and high surface roughness. The current work aims at developing ALD of Ru using an O_2 plasma in order to improve the film nucleation and to try to obtain smoother films. Using the novel $CpRu(CO)_2Et$ precursor and O_2, both thermal and remote plasma ALD of Ru were studied in the same reactor at wafers up to 200 mm. Unlike thermal ALD, the Ru film growth by remote plasma ALD does not rely on the dissociative chemisorption of O_2 on the Ru surface and good film nucleation is expected by providing O radicals from the gas phase. *In situ* spectroscopic ellipsometry, x-ray reflectometry and diffractometry, and electrical measurements clearly show this benefit of the O_2 plasma. The Ru films almost immediately nucleate for the plasma-based process, whereas the thermal process showed a nucleation delay of approximately 100 cycles. Once the film growth has started, the growth per cycle (1 Å/cycle), the electrical properties (20 µΩcm for >5 nm films), and the polycrystalline structure are similar for both ALD processes. However, despite the drastically improved nucleation, the remote plasma ALD Ru films show higher roughness values than the thermal ALD Ru films (roughness of 13 nm and 8 nm for 20 nm thick films, respectively). To elucidate this unexpected phenomenon, the film nucleation and surface reactions were examined. Mass spectrometry provided insight into the reaction products (CO, CO_2 and H_2O mainly) and, therefore, into the surface chemistry ruling both ALD processes. Optical emission spectroscopy delivered information on the species created during plasma exposure. A reaction mechanism will be proposed for these oxygen-based ALD Ru processes that accounts not only for the differences in nucleation, but also relates to the roughness development of the Ru films.

10:00am **TF2-MoM6 Atomic Layer Deposition of Platinum-Iridium Mixed Metal Layers**, ***J.W. Elam***, *S.T. Christensen*, Argonne National Laboratory

Atomic layer deposition (ALD) provides the unique and powerful capability to blend materials at the atomic scale for tuning and optimizing the properties of the resulting mixed layers. The ALD of mixed metal-oxide layers to maximize the charge storage capacity of dielectric materials is well known, but the ALD of mixed metal films is less well explored. The capability to synthesize mixed-metal layers with tunable physical and chemical properties could benefit numerous applications such as catalysis, hydrogen storage, corrosion resistance, and microelectronics, and the ALD of metal laminate nanostructures offers the possibility of core-shell structures and near surface alloys. In this study, we examine the ALD of platinum-iridium (Pt-Ir) mixed metal layers. The platinum ALD uses alternating exposures to (methylcyclopentadienyl) trimethylplatinum and oxygen while the iridium ALD uses alternating exposures to iridium(III) acetylacetonate and oxygen. The similar chemistries and process conditions for these pure metals facilitates ALD of the mixed metal layers. Furthermore, the tendency of Pt to form discrete nanoparticles on oxide supports makes this material attractive for catalytic application. We examined the Pt-Ir mixed metal ALD using in situ quartz crystal microbalance and quadrupole mass spectrometer measurements to investigate the growth mechanism for the pure and mixed materials as well as the effect of mixing on the metal nucleation and growth. In addition, ALD Pt-Ir films were prepared on planar substrates and examined with a variety of techniques to evaluate the thickness, morphology, crystal structure, and chemical composition of the films. These results demonstrate that the thickness and composition of the Pt-Ir films can be controlled precisely.

11:00am **TF2-MoM9 Electrically Conductive Fiber Media by Atomic Layer Deposition of Tungsten**, ***J.S. Jur***, *J.-S. Na, G.N. Parsons*, North Carolina State University

The ability to create electrically conductive fiber mats and bundles, woven fabrics, and engineered polymer structures offers unique possibilities for emerging technologies such as sensors, optical and radio wave shielding, flexible heating elements, liquid and gas permeation, as well as new platforms for renewable energy devices. Conductive fiber systems have been largely been confined to the use of metal particle fillers and use of the conductive polymers that limit the properties of the fiber media. Here we report the use of atomic layer deposition (ALD) of tungsten using WF6 and Si2H6 as a precursor and reactant, respectively, as a novel and systematic method to conformally coat an electrically conductive material on complex fiber architectures. By ALD processing, a uniform coating of tungsten was achieved at a temperature of 180 °C on quartz tissues with fibers ranging in diameter from 250 nm to 3 µm. A deposition rate of 3.4 Å/cycle was measured by deposition of tungsten on Si coated with ~80 Å of ALD Al2O3. The tungsten growth nucleation period on the quartz tissue is predicted to be similar to tungsten growth on Al2O3. Scanning electron microscopy showed only minor cracking of the tungsten film coating on the quartz fibers, even after handling. The resistivity of ALD tungsten thin films grown on Al2O3 was < 200 µOhm cm, and measurements show similar resistivity values for the tungsten deposited on the quartz fiber. Electronic transport differences in measurement of resistivity and the subsequent mechanisms for conductive pathways through fiber bundles compared to monolithic structures will be discussed. These results suggest new opportunities in the use of ALD processing to create electronically active fiber systems.

11:20am **TF2-MoM10 Interconnect Reliability Improvement by Selective CVD of Co Capping Layer on SAM Treated Copper/Low-k Surface**, ***H.B. Bhandari***, *H. Park, R.G. Gordon*, Harvard University

Electromigration in copper interconnects is a surface phenomenon and therefore becomes a dominant reliability concern as the Cu line widths are narrowed to accommodate the continuing scaling of interconnect structures. Reliability can be improved by applying a layer of cobalt metal on the top surface of Cu lines, thereby improving its adhesion to an overlying etch-stop layer such as silicon nitride. Thus selective deposition of Co metal on ultra narrow Cu lines integrated in low-*k* dielectric is of critical importance in preserving the electrical performance of future integrated circuits. Here we propose a chemical vapor deposition process for applying Co thin films selectively on Cu surfaces. XPS showed complete coverage by Co films less than 2 nm thick on Cu substrates. The selectivity of the Co deposition was confirmed by Cu line to line leakage measurements on long interdigitated comb structures. Further enhancement of Co selectivity was achieved by employing self-assembled monolayers (SAMs) to passivate low-*k* surfaces. XPS and TEM characterizations indicate that low-k surfaces treated with (heptadecafluoro-1,1,2,2,-tetrahydrodecyl)trimethoxysilane or (heptadecafluoro-1,1,2,2,-tetrahydrodecyl)dimethyl(dimethylamino)silane inhibited Co nucleation on insulators. Clean Cu surfaces were unmodified by the SAM treatment. The selective passivation was investigated using both solution- and vapor-based SAMs to obtain complete blocking of Co deposition on low-k surfaces.

11:40am **TF2-MoM11 From Chemisorption to Steady-State Growth: Initial Stages of ALD Examined using *In Situ* X-ray Photoelectron Spectroscopy**, ***K.J. Hughes***, *J.R. Engstrom*, Cornell University

One of the least understood aspects of atomic layer deposition (ALD) is the initial stage of growth, which involves the first set of reactions between the thin film precursors and the substrate. As ALD growth is invariably conducted on foreign substrates, the surface must evolve from that representing the starting substrate, to that eventually representing the steady-state growth surface. Here we employ *in situ* x-ray photoelectron spectroscopy (XPS) to examine the initial stages of growth of TaN_x from the reactions of $Ta[N(CH_3)_2]_5$ and NH_3 on SiO_2, porous low-κ substrates, and both of these substrates modified with interfacial organic layers (IOLs). In this presentation, first, we will examine the effect of the density of the reactive adsorption sites (-OH groups) on SiO_2 and SiO_2 based porous low-κ substrates. Here we find that the saturation density (coverage) of Ta depends strongly on the initial density of –OH. Moreover, we find that there is a strong correlation between the amount of ligand loss in this first half-cycle, and the density of the reactive adsorption sites. For example, on porous low-κ substrates, reactions involving the loss of a single ligand and formation of $–O\text{-}Ta[N(CH_3)_2]_4(a)$ species dominate. In contrast, on surfaces with a high density of –OH (SiO_2), ligand loss is much more significant. Second, another important feature that XPS can probe is the chemical state of the primary thin film constituents. One process observed in the first cycles of growth is the shift in the position of the N(1s) peak, from a binding energy of *ca*. 398.9 eV to 397.2 eV. The former binding energy corresponds well to that reported for $–\underline{N}(R)_2$ species (398.6), while the latter is close to that reported for $Ta\underline{N}$ (397.5) and $Ta_3\underline{N}_5$ (396.9). As a final example, we will consider growth of TaN_x on SiO_2 and porous low-κ substrates modified with interfacial organic layers. We have found that adsorption of a branched polymer possessing a high density of $–NH_2$ species on the porous dielectric increases both the initial uptake of $Ta[N(CH_3)_2]_5$ in the first half cycle, and the growth rate per cycle. Here an important issue concerns the fate of the IOL—does the ALD thin film quickly and uniformly cover the IOL, or are there reactions between the ALD precursors and the IOL? We find that the fate of the IOL depends strongly on the density and spatial distribution of reactive groups in the organic layer. We will discuss the implications of these observations concerning the use of IOLs as nucleation promoters in ALD.

Vacuum Technology
Room: C1 - Session VT-MoM

Vacuum Contamination and Pumping
Moderator: M. Wüest, INFICON Ltd., Liechtenstein

8:20am **VT-MoM1 Silicon-based Surface Treatments for Improved Vacuum System Throughput, Inertness, and Corrosion Resistance**, ***D.A. Smith***, SilcoTek Corporation, *B.R.F. Kendall*, Elvac Associates **INVITED**

Tests of stainless steel components with a silicon-based deposition have shown significantly lower outgassing rates when compared with stainless steel components without a surface deposition. A variety of experiments illustrate the beneficial aspects of a silicon-based deposition in process vacuum systems. For outgassing performance, experimentation was developed for comparing otherwise identical samples having various surface treatments and/or coating types. The samples are heated and cooled in turn while the outgassing rates are recorded at temperatures up to 250 degrees C. For inertness performance, chromatographic and gravimetric data will illustrate the lack of adsorptive and catalytic behavior of a substrate with a silicon-based deposition. These depositions can also serve as an anti-corrosive barrier for processes hindered by frequent maintenance after exposure to environments that are corrosive to base materials. ASTM corrosion testing methods will be presented and discussed to better understand the anti-corrosive nature of these deposited surfaces. Process vacuum systems requiring rapid pumpdown, minimal metallic substrate exposure and contamination, and/or reduced corrosive attack may benefit from the characteristics capable with silicon diffusion coatings.

9:00am **VT-MoM3 Modeling Decontamination of Vacuum Chambers by Downstream Plasma Cleaning**, ***C.G. Morgan***, *R. Vane*, XEI Scientific, Inc.

Downstream plasma cleaning is an effective means for removing carbon contamination from vacuum chambers. The downstream plasma cleaning device is mounted on an unoccupied port on a vacuum chamber. When in use, the device creates oxygen radicals using a small leak of oxygen containing gas and a low power (5-20 W) radio frequency (RF) plasma. The oxygen radicals then flow through the vacuum chamber, ashing hydrocarbons. The rate of carbon decontamination has been shown to be dependent on a number of factors: RF power level, chamber pressure and geometry, distance between radical source and contamination, speed of the pumping system, and type of oxygen containing gas used. Decontamination rates can be accurately estimated if chemical models of both the oxygen radical reactions within the chamber and on the contaminant surface can be developed. These models are validated by physical data from two experiments varying the parameters listed above.

Data is presented from two experiments with oxygen radicals. Both experiments use a quartz crystal microbalance (QCM). In the first, a silver-coated QCM is placed in the vacuum chamber and subjected to the plasma cleaning process. Oxygen radicals will incorporate themselves into the QCM and increase its mass. The flux of oxygen radicals impinging on the QCM surface can be calculated using the Deal-Grove model of surface oxidation. By locating the silver-coated QCM in different locations of a vacuum chamber, a map of oxygen radical concentrations as a function of distance from the plasma can be made. In the second, a gold-coated QCM is contaminated with hydrocarbons. Test contamination is achieved by heating a small amount of hydrocarbon in a vacuum chamber and allowing the evaporation to recondense on the gold-coated QCM. The cleaning process is then initiated and an experimental trace showing mass loss from the gold-coated QCM as a function of cleaning time is obtained.

A chemical box model which assumes that once the plasma is lit there is a steady-state oxygen radical concentration within each box can be compared to the data from the silver-coated QCM experiments. The chemistry within each box is obtained by using a standard database of gas phase reaction rates. The second model focuses on the gas surface chemistry of decontamination. The results of the second model are compared with the data from the mass loss traces of the gold-coated QCMs. The combination of both models will provide a means to estimate rates of downstream plasma cleaning for any contaminated vacuum system.

9:20am **VT-MoM4 Methods for Measuring Outgassing for Qualification of Materials, Components and Systems**, ***N.B. Koster***, *R. Koops, E. van Zeijl*, TNO Science and Industry, Netherlands

Presently cleanliness requirements for vacuum systems in use for Extreme Ultra Violet Lithography (EUVL) are beyond what with standard procedures can be achieved. Especially the constraint that the system cannot be baked after assembly, whilst cleanliness better than UHV is needed, requires special measures with respect to manufacturing and qualification. Because of the constraint of not being able to bake the system we refer to this type of vacuum as Ultra Clean Vacuum (UCV). This presentation will focus on outgassing measurement methods for qualification of materials and components. Traditionally only the total outgassing is measured and reported, as can be found in many vacuum handbooks. In the case of EUVL, or other systems with high energetic particles, we distinguish several species of interest, like water and hydrocarbons and provide numbers for outgassing of these species as measured with a RGA. These measurements enable engineers to calculate total pressure and cleanliness of a system under design. Results of these measurements will be shown including a way of representing the data in a clear format. We also will show results of a new method for measuring hydrocarbon outgassing with the aid of a RGA when the outgassing levels are at the lower detection limit of the RGA.

9:40am **VT-MoM5 Outgassing Characterization of Elastomeric Seals Used in Semiconductor Wafer Processing**, ***M. Heller***, *S. Sogo, J. Chen, J. Legare*, DuPont Performance Elastomers L.L.C.

Many integrated circuit manufacturing processes operate in high or ultra high vacuum (UHV) environments. It is important that vacuum levels are maintained within specified limits to insure optimum process efficiency. While specification of an appropriate size vacuum pump for the system can insure that overall vacuum levels are maintained, outgassing from sealing materials can interfere in the process by changing the composition and morphology of the deposited layer. For instance, outgassing contaminants absorbed by the exposed substrate during the initial steps of the deposition process can induce undesired interactions at the interface level and consequently affect the grown film as well as the overall process. Therefore, it is important to understand the outgassing characteristics of elastomeric seal materials in order to select the appropriate material for a given application.

A methodology has been developed using a residual gas analyzer to measure the outgassing properties of elastomers. Results indicate that outgassing typically takes place in two stages. With some minor exceptions, the first stage involves the evolution of atmospheric gasses and absorbed moisture (i.e. nitrogen, water, oxygen, and carbon dioxide). The second stage and possibly of greater interest involves the evolution of gasses related to the thermal stability and decomposition of the material in question.

This paper compares the outgassing characteristics of three different types of elastomeric seals (perfluoroelastomers, fluorelastomers and silicones) typically used in semiconductor wafer processing. Data on outgassing rate as a function of time and temperature, and classification of gas species evolved for products in each material class are presented. While perfluoroelastomers offer the lowest outgassing rate at elevated temperatures, there can be some performance variation within this material class. The relationship between outgassing performance and elastomer formulation will also be discussed.

10:00am **VT-MoM6 Permeation Through Elastomers: Comparison of Viton® and Chemraz® 653 O-rings under Controlled Compression and Temperature**, ***N.T. Peacock***, MKS Instruments, HPS Products

Many types of elastomers are available and used for demountable seals in vacuum service. One important consideration in the selection of the elastomer material is the permeation rate. The permeation rate for gasses like helium can differ by orders of magnitudes for different seal materials. In this study, the gas load through a single O-ring due to permeation was compared for Viton® E and for Chemraz®653. The procedure was to use a MSLD (mass spectrometer leak detector) with helium and log the leak signal at intervals often a few seconds apart as a controlled flow of helium was applied to the seal. This was done both at room temperature and at elevated temperatures up to 140o C. The test O-ring was located in a specially constructed fixture that allowed an O-ring to be compressed to five different values ranging from 15% to 27% compression. Leak signals due to permeation through the 2-227 sized O-ring (nominal 0.139 inch cross section) were found to vary by orders of magnitudes. For instance at 22% compression and room temperature, the peak leak signal from the Viton® seal was approximately 1x10-10 mbar-l/sec while for the Chemraz®653 seal it was approximately 2x10-8 mbar-l/sec. When the seals were at 140o C with the same compression, the leak signals became approximately 1x10-8 mbar-l/sec for the Viton® and approximately 8x10-7 mbar-l/sec for the Chemraz®653 seal.

Leak signals due to permeation of these magnitudes are very important when troubleshooting or qualifying equipment since leak rate specifications on equipment are often lower. The same set up was also used to help find ways to distinguish a response on the leak detector due to a leak from a signal due to permeation. Using the rapid data recording and graphical display of the leak signal, it was found that permeation responses had a characteristic shape. With a response due to permeation, there is a short time before the response starts, a ramp up time, and then a slow decay. By contrast, signals from known leaks were shown to have a very rapid response time, and a quick decay or ‘clean up’ when the probe gas was removed. Using a graphing display, and comparing the response to known examples, operators can distinguish the two situations.

10:40am **VT-MoM8 Controlled Formation of Condensed Frost Layers in Cryogenic High Vacuum Pumps**, ***S.E. Syssoev***, *A.J. Bartlett, M.J. Eacobacci*, Brooks Automation Inc.

Cryogenic high vacuum pumps are used on a wide variety of vacuum substrate processing equipment, space simulation systems, and analytical instruments. They produce high pumping speeds for all gases and work over a wide range of pressures. Pumping residual gases occurs by cooling them to the point that they condense on the appropriate cryogenic surface. Thus, the pumping speed of the cryopump can be converted into deposition rate of the pumped gases onto cold surfaces inside the pump. The thickness of the deposited layer is uneven due to geometry of the cryopanels inside the pump. The majority of the trapped gas forms thick and comparable stable amorphous structures, while a significantly smaller amount of the pumped gas is participating in low rate deposition on those zones inside the pump that are less exposed to the gas flow. This low rate deposition leads to formation of polycrystalline films with complicated crystallographic structure even for the simple binary gas mixture widely used in the most applications in semiconductor industry. As with any thin film, this type of polycrystalline frost can be subject to appreciable residual stress due to structural defects. The concentration of such defects depend on operating conditions such as pumped gas composition, pressure, rate of deposition, and condensation temperature. For the stressed film there is always a certain film thickness (critical thickness, [1]) after which the film can exhibit one of the possible cracking pattern – surface crack, channeling, or debond. Defects in the condensed solid gas films grown inside the cryopump can lead to spontaneous delamination resulting in frost flakes being ejected from the array surface with subsequent sublimation on the warmer surfaces of the pump. Sporadic sublimation of delaminated flakes lead to unwanted pressure variations, or bursts, inside the vacuum system. This report discusses the types of film formations found in a typical cryopumping array structure and summarizes the development of a new cryopump with increased capacity and elimination of sporadic pressure bursts occurring during the cryopumping of type II gases. The pump employs the GM refrigeration cycle and is a further modification of the Brooks Automation On-Board IS 8F cryopump [2]. The test results showing pressure bursts free operation and 50% higher capacity for type II gas achieved with no changes to cryopump external geometry are presented and discussed.

[1]. J.Hutchinson et al. *Mixed mode cracking in layered material*. Advances in applied mechanics, 29, 63 (1992).

[2]. A.J.Bartlett et al. *Pressure burst free high capacity cryopump.* United States Patent Application 20080168778, (2008).

11:00am **VT-MoM9 Combination of Compact NEG and Small Ion Pumps for UHV Systems**, ***P. Manini***, SAES Getters, Italy, *C.D. Park, S.M. Chung*, Pohang Accelerator Laboratory, South Korea

Achieving a better base pressure and reducing bake-out time are the two important practices for an UHV system. Use of a sputter ion pump (SIP) in combination with non-evaporable getter (NEG) is one of the good solutions for this. Although many efforts have been made showing results of the pumping performances of NEG-SIP combination, the SIPs used were relatively large. Furthermore there is a demand for high performance, compact combination pumps that can be installed in a tight space in a storage ring of the proposed PLS-II project. Thus we tested the characteristics of a compact NEG-SIP combination pump (CNP) to see if the CNP can meet the above mentioned desires.

A compact getter cartridge mounted on CF40 flange (Capacitorr D 400-2) was used in combination with small SIPs, having speeds ranging from 10 to 60 l/s. The CNP was attached to a stainless steel chamber that has five CF40 flanges with a total inner surface area of 3,000 cm^2.

Base pressures (BPs) of the CNP-UHV system, in a wide range of situations, with/without NEG and with/without baking were measured. Significantly lower pressures and faster pumping could be achieved using the CNP. Base pressures of low 10^{-11} mbar could be obtained with a compact NEG for 10 l/s and 60 l/s SIPs after a 48-h bakeout.

The results also show that the compact CNP can provide high pumping speed and reach 10^{-11} mbar after a very short (few hours) bakeout. The BP was $1\text{x}10^{-10}$ mbar with 60-l/s SIP alone after a 48-h bakeout, whereas it was $7.9\text{x}10^{-11}$ mbar with the CNP; a better result after only 2-h bakeout. This is quite a remarkable decrease in the bakeout time of a UHV system.

It is worthwhile to note that UHV could also be achieved with the CNP even in a fully unbaked system: A pressure of $3.9\text{x}10^{-10}$ mbar with the CNP was reached, while it was $8\text{x}10^{-9}$ mbar with the SIP alone. The other interesting result of the CNP-UHV system is that the pressure increase is much less and slower when the SIP is switched off. This is also a good characteristic, required for portable vacuum devices.

All these characteristics are particularly useful for the design and operation of the vacuum system of a storage ring. It may also be beneficial for the miniaturization of vacuum equipments and mobile applications which require smaller pumping systems.

11:20am **VT-MoM10 Water Vapor Cryopumping: Refrigerant Phaseout Compliance**, ***K. Flynn***, *C. Rebecchi*, Brooks Automation Polycold Systems

Water vapor cryopumps, which use mixed gas refrigeration technology, rely on mixtures containing four or more refrigerants, each with widely spaced boiling points. Historically, these mixtures contained two or more chlorinated refrigerants such as chlorofluocarbons (CFC's) or hydrochlorofluorocarbons (HCFC's). Both classes of compounds contribute to depletion of the stratospheric ozone layer and are subject to legislative action to phase out these compounds. CFC refrigerants were banned in the US and other developed countries in 1995. HCFC refrigerants are currently in use, but are targeted for phase out. Mixed gas refrigerant water vapor cryopumps have relied on HCFC refrigerants, including HCFC R-22 since the early 1990's when CFC refrigerants were phased out. Although water vapor cryopumps experience much lower leakage rates than commercial refrigeration systems, they are subject to the same laws as all other refrigeration equipment. Effective January 1, 2010, the use of R-22 will be banned on new equipment in the US. R-22 is a key refrigerant in water vapor cryopumps due to its excellent refrigeration capacity and its relatively low freezing point (-160 °C). The phase out of R-22 has required extensive development of alternative refrigerants. It has been accomplished for three important sizes of water vapor cryopumps. The resulting products provide water vapor cryopumping at the same speeds and water vapor partial pressures as the previous mixtures with R-22. This paper reviews the development approach, and compares system and pumping performance for these green products. Experimental data from commercial vacuum systems is presented for the old and new product.

11:40am **VT-MoM11 Vacuum Processing for the 21st Century**, ***S. Ormrod***, *N. Schofield*, Edwards Ltd, UK

On the 90th anniversary of the foundation of Edwards by FD Edwards, the origins of industrial vacuum processing are examined. They are then compared with progress at the time of FD Edwards' death in 1966 and finally, possible developments are examined in the light of vacuum processing technology in 2009.

Proliferation of vacuum processes are shown to drive the evolution from mercury based vacuum technology through oil sealed pumping to dry pumping in the primary and secondary pumping pressure region resulting in a significant market for vacuum processing equipment.

Looking ahead, likely commercial influences are identified, such as electronic, environmental, and safety applications.

To meet that demand, trends and limitations in vacuum engineering are highlighted, particularly capacity, power and rotational speed. The benefits of applying electronics to vacuum processing become apparent - the very products vacuum processing equipment has helped to manufacture so successfully.

Applied Surface Science
Room: C2 - Session AS+EM+MS+TF-MoA

Spectroscopic Ellipsometry II
Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

2:00pm **AS+EM+MS+TF-MoA1 Spectroscopic Ellipsometry on Protein Layers: Characterization and Sensor Applications**, ***H. Arwin***, Linköping University, Sweden **INVITED**

Ellipsometry is very attractive for studies of biolayers including protein layers. First, its thickness resolution is well below 1 nm which is perfect for protein layers as they typically are composed of nm-sized molecules. Second, ellipsometry can be used in any transparent medium, so it can be applied to solid-liquid interfaces where many bioreactions take place. Third, molecules do not have to be labeled, as required for techniques based on fluorescence or radioactivity. One drawback is that it is not analytic if operated in the visible spectral range and in simple applications one primarily measures the optical mass on a surface. However, with high precision spectroscopic ellipsometry, structural information in protein monolayers can be obtained in some cases and chemical analysis can be performed with infrared ellipsometry.

In this report, the use of various types of ellipsometry for studies of protein layers at air/solid and liquid /solid interfaces are reviewed. Among the methods included are spectroscopic, dynamic, internal reflection and imaging ellipsometry. Two examples of methodology for analysis are discussed in some detail. First we observe that *in situ* studies allow monitoring of the dynamics of protein layer growth. Modeling of layer structure by separation of refractive index and thickness from such *in situ* data recorded during adsorption of fibrinogen layers is presented as well as strategies for evaluation of surface mass density.

In a second example, a model dielectric function (MDF) concept for protein layers in the UV-VIS-IR spectral range is presented. The MDF contains model parameters like resonance energies and broadenings of vibrational structures, e.g. in the amide bands. Changes in these parameters can be monitored and used to assess the conformational state in the protein layer. As an example, studies of thermally induced degradation of fibrinogen layers are presented.

Finally potential sensor applications based on imaging and dynamic ellipsometry utilizing sub-nm thickness resolution are reviewed. The use of surface-plasmon resonance enhancement to increase resolution of internal reflection ellipsometry to pm in thickness will be discussed.

2:40pm **AS+EM+MS+TF-MoA3 Anisotropic Optical and Magneto-Optical Properties of Sculptured Thin Films**, ***D. Schmidt***, *T. Hofmann, A. Kjerstad, E. Schubert, M. Schubert*, University of Nebraska-Lincoln

Three-dimensional structure design on the nanoscale is in the focus of modern material science and engineering because intriguing applications are foreseen for such nanostructured films in various fields ranging from optics, electromechanics or electromagnetics. We utilize glancing angle electron-beam deposition, where physical shadowing and varying particle incidence azimuth are exploited for fabrication of three-dimensional individual nanostructures arranged in sculptured thin films with different morphologies. We will present the anisotropic (structure-related) optical and magneto-optical properties of sculptured thin films from cobalt. Generalized spectroscopic ellipsometry is employed to determine the anisotropic principal optical constants of slanted columnar and chiral nanocoil thin films in the spectral range from 400 to 1650 nm. These thin films show strong form birefringence and large dichroism and are distinctly different from their bulk material. We will also discuss why slanted columnar thin films have monoclinic optical properties [1]. Magneto-optic Kerr effect measurements in the polar configuration lead to the determination of the magneto-optical Q-values (Voigt parameters) of such highly anisotropic ferromagnetic sculptured thin films.

[1] D. Schmidt, A. C. Kjerstad, T. Hofmann, R. Skomski, E. Schubert, and M. Schubert, J. Appl. Phys. **105**, XXX (2009).

3:00pm **AS+EM+MS+TF-MoA4 Development of Hybrid Quartz Crystal Microbalance / Ellipsometric Porosimetry for the Characterization of Anisotropic Optical Materials**, ***R.A. May***, *D.W. Flaherty, C.B. Mullins, K.J. Stevenson*, University of Texas at Austin

Ellipsometric porosimetry (EP) relies on monitoring the change in optical properties during vapor adsorption/desorption and has been successfully applied to an array of materials using a variety of adsorbates both in vacuum and at ambient pressures. However, these studies typically avoid the analysis of optically complex systems with strong absorbance or optical anisotropy. Towards this end, a hybrid quartz crystal microbalance/ ellipsometric porosimetry (QCM/EP) technique is being developed to facilitate the study of more complex optical materials and to quantitatively estimate parameters such as porosity, pore size distribution, and surface area. To highlight the power of this hybrid approach thin films of TiO_2 and TiC, have been deposited using reactive ballistic deposition (RBD). RBD provides control over film parameters such as surface area, porosity, pore size, and birefringence through variation of the deposition angle. Combined with the QCM/EP technique these films provide a platform for understanding both novel material properties and the requirements for extracting valid optical constants from anisotropic optical materials.

3:40pm **AS+EM+MS+TF-MoA6 Multichannel Ellipsometry for Thin Film Photovoltaics Applications: From Materials to Solar Cells**, ***R.W. Collins***, *J. Li, M.N. Sestak, J.A. Stoke, L.R. Dahal*, University of Toledo **INVITED**

Second generation or thin film photovoltaics (PV) technologies have achieved the lowest manufacturing costs in the PV industry. These technologies benefit from multichannel ellipsometric analysis for characterization of multilayered thin film materials and deposition processes, specifically for determination of component layer thicknesses and dielectric functions. From such results, predictions of the maximum achievable quantum efficiency of multilayered PV device structures are possible. In this presentation, the current applications and future prospects of multichannel spectroscopic ellipsometry (SE) will be discussed for optical characterization of PV materials and devices during fabrication in the research laboratory as well as for on-line and off-line evaluation in PV module production. First, this review will address the advances in instrumentation for multichannel SE. Second, this review will provide examples of the analysis of real time SE data acquired during film growth to obtain structural parameters and dielectric functions, as well as the subsequent analysis of the resulting dielectric functions in terms of parameterized models to deduce useful information on thin film materials properties. Recent applications to be discussed in this presentation involve (i) the analysis of grain size, strain, and void profiles from the dielectric functions of polycrystalline CdS and CdTe thin films used as heterojunctions in efficient solar cells; (ii) the analysis of amorphous and nanocrystalline volume fraction profiles from the dielectric functions of mixed-phase hydrogenated Si (Si:H) thin films also used in efficient solar cells; and (iii) the determination of interface dielectric functions and losses associated with Ag/ZnO structures used as back-reflectors in efficient thin film Si:H PV devices. In the latter studies, the optical features of confined plasmon resonances can be identified. Methods for dealing with microscopic (sub-wavelength order) and macroscopic (wavelength order) surface and interface roughness will be treated, as will its impact on prospects for analyzing PV device structures on-line during module manufacturing. The ability to extract polarization, depolarization, and irradiance information from the reflected beam by multichannel SE is advantageous in many such PV applications.

4:20pm **AS+EM+MS+TF-MoA8 Universal Behavior of Light Scattering from Self-Affine Fractal Surfaces: A Quantitative Relationship between Roughness and EMA Models**, ***A. Yanguas-Gil***, *B.A. Sperling,* University of Illinois at Urbana-Champaign*, J.R. Abelson*, University of Illinois, Urbana-Champaign

The effective medium approximation (EMA) is typically used to model the influence of roughness on the optical response of a surface or buried interface as measured by ellipsometry. Although the standard assumption of 50% material - 50% void provides useful results, the relationship between the EMA layer thickness and the surface topography is not fully understood. For example, in thin film deposition many authors have found a good correlation between the thickness of the EMA layer and the rms surface roughness measured by AFM, while others have found significant discrepancies between the time evolution of these two parameters.

Using first principles scattering models, we have analyzed the ellipsometric response of surfaces that exhibit a self-affine dependence of surface topography on the lateral scale of measurement. This type of surface roughness is found for a wide variety of real surfaces, including many deposited thin films. The calculations show that when the surface correlation length evaluated from the height-height correlation function or the power spectral density is much smaller than the incident wavelength, a universal behavior is found in the ellipsometric response. Both the amplitude of the reflected fields in the p- and s-polarizations, and the thickness of the EMA layer, depend on the product of the *rms* surface roughness times the average surface slope. Therefore, the linearity between roughness and the thickness of the EMA layer holds only as long as the average surface slope remains constant. That is the case when the growth obeys the predictions of dynamic scaling theory, i.e., the *rms* roughness and the correlation length change with time as $\sigma \sim t^{\beta}$ and $\xi \sim t^{\beta/\alpha}$, where α and β are the roughness and the growth exponents, respectively. Results are presented for different materials whose optical properties cover a broad range from metals to dielectrics. An important consequence of this universality is that the ellipsometric response is mathematically separable into two independent functions, one depending only on the optical properties of the film and the other only on the surface topography.

4:40pm **AS+EM+MS+TF-MoA9 Numerical Ellipsometry: Thin Absorbing Films Deposited on Opaque Substrates**, ***F.K. Urban***, *D. Barton,* Florida International University*, T.E. Tiwald*, J A Woollam Co.

A major challenge for those utilizing ellipsometry is numerical processing of the measured data. The transcendental, multivalued equations arising from the physics of simple reflection are problematic for the least-squares numerical methods in common use. These early numerical methods require fairly accurate initial estimates, bounding to avoid local minima, and only find solutions at the bottom of a relatively flat numerical topography. Previously we have applied Complex Analysis in the n-k plane to improve visualization of the mathematics and this has led to a growing array of new numerical methods avoiding these difficulties. The work presented here extends these new numerical methods for use beyond transparent substrates to include absorbing substrates. Results show that reflection ellipsometry alone can be sufficient for determination of thin absorbing film thickness and optical properties without the need for additional kinds of measurements.

Numerical processing considering surface layers such as air-formed oxides will also be presented.

5:00pm **AS+EM+MS+TF-MoA10 *In situ* Spectroscopic Ellipsometry As a Versatile Tool to Study Atomic Layer Deposition**, ***E. Langereis***, *H.C.M. Knoops, W. Keuning, A.J.M. Mackus, N. Leick, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, The Netherlands

Atomic layer deposition (ALD) is considered as one of the primary candidates for the deposition of ultrathin and conformal films with precise growth control. In this contribution, the merits of using *in situ* spectroscopic ellipsometry (SE) to address various aspects of ALD will be discussed. In particular, the versatility of this all-optical diagnostic will be demonstrated by results obtained on metal oxide (Al2O3, HfO2, Er2O3, TiO2, Ta2O5, and SrTiO3), metal nitride (TiN and TaN*x*), and metal (Pt and Ru) films with thicknesses ranging from 0.1 to 100 nm [1]. By acquiring SE data within a combined photon energy range of 0.75-6.5 eV in between the ALD (half-)cycles and by analyzing the film thickness and the energy dispersion of the optical constants of the films, the layer-by-layer growth and material properties of the films can be studied in detail. It will be shown that the growth rate per cycle and the ALD saturation curves can be determined directly by monitoring the film thickness as a function of the number of cycles, while also the nucleation behavior of the films on various substrates can be probed. Furthermore, it is demonstrated that the energy dispersion relation can provide information on the optical properties, the crystalline phase, and the material composition of the films. For metallic films, electrical properties can be calculated from the Drude absorption yielding insight into the electrical resistivity and electron scattering effects in ultrathin films.

[1] E. Langereis et al., J. Phys. D: Appl. Phys. 42, 073001 (2009).

5:20pm **AS+EM+MS+TF-MoA11 Mueller-Matrix Ellipsometry Studies of Optically Active Structures in Scarab Beetles**, ***K. Järrendahl***, *J. Landin, H. Arwin*, Linköping University, Sweden

Ellipsometry is a valuable tool for general materials characterization but also for optical investigations of complex structures including multilayers, photonic crystals, metamaterials and other artificial materials. The complexity of these kind of structures has during the years promoted the use of spectroscopic, variable angle, generalized and Muller-matrix ellipsometry. In parallel more complex optical models and analysis algorithms have come into use.

Naturally occurring structures may show even higher complexity than artifical structures but with a more narrow range of constituent materials, mainly chitin and various proteins. Many interesting structures are found in insects, especially in butterflies and beetles. Fascinating reflection properties result from intricate photonic structures in their wing scales and cuticles. Currently there is a large interest to explore such functional supramolecular architectures for exploitation in nanotechnology.

Even though the optical properties of natural structures are frequently investigated, ellipsometry rarely has been used to reveal structural and optical properties. In this study, Mueller-matrix spectroscopic ellipsometry is applied in the spectral range of 300 to 1700 nm to investigate structures in the cuticle of Scarab beetles, primarily *Cetonia aurata* (the rose chafer). The cuticle of *Cetonia aurata* is green with a metallic look and reflects circular polarized light. It has been suggested that the circular polarization of this metallic gloss is caused by a helical structure in the chitinous cuticle. We find that the circular polarization effect is limited to the narrow spectral range 470-550 nm and for shorter or longer wavelengths the reflection properties are similar to those from a near-dielectric material. Furthermore, the light reflected from *Cetonia aurata* is left-handed circularly polarized and the beetle thus appears black if viewed through a right-handed circular polarizer. In addition to Mueller-matrix spectroscopic ellipsometry, reflectance and scattering measurements are used to characterize the cuticle of *Cetonia aurata*. Model calculations and parameterization of the nanostructure employing a heliocoidal structure are discussed.

Biomaterial Interfaces
Room: K - Session BI-MoA

Protein and Cell Interactions at Interfaces I
Moderator: T. Boland, Clemson University, B.G. Liedberg, Linköping University, Sweden

2:00pm **BI-MoA1 Bioengineering Stem Cell Fate**, *H.M. Blau,* ***K. Havenstrite***, Stanford University **INVITED**

A major challenge facing stem cell biologists is an understanding of the mechanisms that direct stem cell fate: the delicate balance between quiescence, self-renewal, and differentiation. Adult stem cells are localized in niches, specialized microenvironments, which protect them from differentiation. Upon culture, adult stem cells lose their “stemness”, or ability to self-renew. We have engineered artificial in vitro microenvironments that mimic key biochemical characteristics of adult stem cell niches in order to analyze the properties of stem cells and influence their fate. Microwell arrays are produced as topographically structured polymer hydrogel surfaces allowing exposure of single cells either to soluble or tethered niche proteins. Using this platform, phenotypic and dynamic analyses of thousands of individual cells can be monitored simultaneously by time lapse microscopy. We have found that single proteins alter proliferation kinetics and asymmetric division behavior, leading to muscle and hematopoietic stem cell self-renewal in culture. Our data demonstrate that parameters of proliferation behavior in vitro correlate with stem cell function assayed in vivo. Ultimately, the goal of these studies is to increase our understanding of stem cell biology, expand stem cells in vitro for clinical applications, and discover new drugs for stimulating a patient’s own stem cells.

2:40pm **BI-MoA3 An Investigation of Human Embryonic Stem Cell Attachment on 496 Different Acrylate Polymers in a Microarray: The Importance of Surface Chemistry as Probed by ToF SIMS**, *M.R. Alexander,* ***J. Yang***, *M.C. Davies,* The University of Nottingham, UK*, Y. Mei, D.G. Anderson, R.S. Langer,* MIT*, M. Taylor, A.J. Urquhart*, The University of Nottingham, UK

The relationship between the surface chemistry of materials and human cellular response has great importance in existing and emerging technology areas such as tissue engineering, regenerative medicine and biosensors. Here, we investigate hESC attachment, surface chemistry (using time of flight secondary ion mass spectrometry (ToF SIMS) and XPS) and bulk properties (using confocal Raman spectroscopy) of a large set of samples with diverse chemistry. These are acrylate polymers in the form of micro-spots in an array made from 22 different acrylate monomers mixed pairwise in different proportions and UV photopolymerised to give 496 unique homo- and co-polymers.[1, 2] We do not find a correlation between the human embryonic stem (hES) cell number and wettability, or surface elemental or functional composition that holds for all the samples on the array. In contrast, surface mass spectrometric data acquired using ToF SIMS correlate strongly with cell attachment on all polymers using partial least squares (PLS) regression. The ability to predict cell attachment using the SIMS data indicated that it contains sufficient information on the surface chemistry of the polymers to describe the effect of surface chemistry on cell attachment. Some of the moieties identified using this approach are consistent with previous theories relating surface chemistry on protein adsorption and in turn to cell adhesion, whereas others are new.

We propose that in the field of cell-material interactions, this result highlights the importance of the molecular information contained in the SIMS spectra in controlling the cell attachment. Furthermore, it indicates how the PLS methodology can be used to identify the relationship between surface chemical moieties represented within the SIMS spectra to complex properties such as cellular response.

[1] D.G. Anderson, S. Levenberg, R. Langer, *Nature Biotechnology*, **2004**, 22, 863-866.

[2] M. Taylor, A.J. Urquhart, D.G. Anderson, R. Langer, M.C. Davies, M.R. Alexander, *Surface and Interface Analysis*, **2009**, 41, 127-135.

3:40pm **BI-MoA6 Design of Protein Polymers as Novel Tissue Engineering Scaffolds**, ***D. Sengupta***, *S.C. Heilshorn*, Stanford University

The ability to tailor specific cell-matrix interactions in biomaterials is now recognized as an important method to control cell behaviour. Biomaterial adhesivity and elasticity are important determinants of cell adhesion, proliferation, and differentiation; and a coordinated cell response to these different material inputs results in complex signaling crosstalk. Independent modification of these biomaterial properties is thus extremely important, but difficult to achieve with current synthetic as well as natural biomaterials. While natural biomaterials such as collagen and Matrigel do not allow for the independent tuning of multiple biomaterial properties, synthetic biomaterials such as PEG and acrylates can be toxic and immunogenic. An alternative approach to natural as well as synthetic materials is the use of protein polymers made with recombinant protein engineering technology. By templating protein synthesis using the genetic code, we have exact molecular-level control over our material. Using this strategy, we have engineered a family of tunable and biodegradable protein-engineered biomimetic materials that incorporate critical elements of the natural extracellular matrix. The materials are manufactured using a modular design strategy, resulting in a fusion protein comprised of multiple peptide domains that provide cell adhesion and matrix elasticity. Specifically, the elastic modulus of the material can be tuned (from ~43-1200 kPa) independently of RGD ligand density (from 0-9300 cell adhesion sites/μm2), enabling optimization of the biomaterial interface for specific tissue engineering applications. Additionally, these interfaces can be easily micro-molded to incorporate micro- or nanoscale topographical features that induce cell alignment. Human embryonic stem cell-derived cardiomyocytes as well as mouse embryonic stem cells cultured on our protein-engineered biomaterials demonstrate viability, proliferation, differentiation, and morphology comparable to positive gelatin controls, providing a viable alternative to commonly used materials. The molecular-level design strategy of these protein polymers allows for unprecedented control over the biomaterial-cell interface for regenerative medicine applications.

4:00pm **BI-MoA7 Axon Guidance on Patterned Gradients of Extracellular Matrix Proteins**, *W. Theilacker, H. Bui,* University of Delaware*, S. Sullivan,* Alcoa Technical Center*, L. Capriotti,* University of Delaware*, D. Willis, J. Twiss,* Alfred I. duPont Hospital for Children*, N. Zander,* Army Aberdeen Research Laboratory*, Z. Zhang,* Excellatron*,* ***T. Beebe Jr***, University of Delaware

This presentation will focus on axonal extension experiments made possible by recent developments in a general platform for substrate patterning of protein and peptide gradients using covalent attachment schemes, and employing cell- and protein-resistant lanes of PEO-like comb polymer. The platform uses step gradients and continuous gradients in local protein and peptide concentrations from micron to centimeter length scales. Control of the local surface density of proteins and peptides allows cell culture assays involving competition of cells for different extracellular matrix (ECM) proteins, propensity of axons to cross from one ECM protein lane into a different ECM protein lane, neuron attachment propensity, axon extension direction and rate, and controlled studies of cell-cell interactions between different cell types. This presentation will address the relationship between the local protein coverage and the "bioactivity" or "bioavailability," using a variety of surface analytical techniques including XPS, TOF-SIMS and AFM, and optical microscopy techniques including epi- and confocal fluorescence microscopy.

4:20pm **BI-MoA8 Aligned Highly Porous Electrospun Scaffolds for Nerve Tissue Engineering**, ***N. Zander***, Army Research Lab/University of Delaware*, J. Orlicki, A. Rawlett,* Army Research Lab*, T. Beebe*, University of Delaware

Spinal cord injuries are one of the most catastrophic and costly types of injuries since damaged axons in the central nervous system are unable to spontaneously regenerate. Although reconstruction of damaged and diseased neural pathways remains a major hurdle, recent research has shown that aligned electrospun fiber mats can provide contact guidance cues to direct axon growth by acting as a bridging device. However, due to the nanometer sized fiber diameter and highly aligned nature of the scaffolds, the low interfiber distance limits penetration of the cells into the scaffold.

To study the effect of fiber mat porosity on cellular infiltration, aligned fiber mats were fabricated via co-electrospinning polycaprolactone with polyethylene oxide (a water soluble polymer). Variation of the fabrication parameters allowed for control of the porosity of the scaffold with a full range of sacrificial (PEO) fiber composition. As the surface composition is also critical in providing biochemical signals to direct neurite growth, the surfaces of the fibers were functionalized via air plasma treatment followed by attachment of several extracellular matrix proteins. The surface chemistry was characterized by X-ray Photoelectron Spectroscopy, Time of Flight Secondary Ion Mass Spectrometry, and Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy. Cellular infiltration, proliferation and neurite outgrowth of PC12 cells were evaluated for fiber mats of varying porosity and surface composition.

4:40pm **BI-MoA9 Study of GPIbα and vWF Interations under Blood Flow**, ***X. Cui***, *HB. de Laat, J. Orje, Z.M. Ruggeri*, The Scripps Research Institute

The mechanism of platelet-adhesion plays an important role in hemostasis and thrombosis. When blood vessels are injured or disrupted, the platelets membrane presented glycoprotein Ibα (GPIbα) will bind to von Willebrand Factor (vWF), which is a large multimeric plasma protein immobilized on collagen fibers. The binding interactions are regulated by the applied fluid shear rates. In this paper, we conducted a study of blood platelets adhesion on vWF A1 domain coated glass slides at different shear rates. The platelets movements are recorded by a high speed camera at 30fps. The recorded videos are analyzed using video/image processing software in order to calculate the platelet velocities at different shear rates as well as different protein coating concentrations. We found the average velocity decreased when the shear rate increased. This showed the binding requires high fluid shear rate in the flow. PLGA beads with the shapes of ellipsoid and sphere of about 1μm diameter were also studied using this method. However, the beads were coated with vWF A1 domain and the flow chambers were coated with GPIbα. We observed the decrease of the velocity with the increased shear rates, which showed increased binding strength between vWF A1 domain and GPIbα protein at higher shear rates. The ellipsoid beads had lower velocity comparing with the sphere beads at the same shear rate due to the larger contact area to the coating surface.

5:00pm **BI-MoA10 Platelets Adhere to Adsorbed Albumin through a Receptor-Mediated Process**, ***B. Sivaraman***, *R.A. Latour*, Clemson University

Since albumin (Alb) lacks known sequences recognized by platelet receptors, it is not supposed to support platelet adhesion. However, studies have suggested that platelets may be able to adhere to adsorbed Alb (*1, 2*) with adhesion related to adsorption-induced Alb unfolding (*1*), although the mechanisms of this remain unclear. To address this issue, we conducted studies to definitively determine if platelets adhere to adsorbed Alb, whether adhesion is related to adsorbed Alb conformation,and if it occurs by a receptor-mediated process. Alb was adsorbed at 0.1, 1.0, and 10 mg/mL on various alkanethiol SAM surfaces to vary the degree of unfolding in the adsorbed Alb. The adsorption-induced conformational changes in Alb was quantified by CD spectropolarimetry (*3*). Platelet adhesion studies were carried out and the platelet response determined by LDH assay and SEM. A series of platelet adhesion inhibitors and protein modification agents were used to probe the mechanisms of platelet adhesion. Platelet adhesion to adsorbed Alb was negligible when adsorbed Alb retained most of its native structure (< 34% loss in alpha-helix), but began to linearly increase with the degree of adsorption-induced unfolding thereafter (r^2=0.92). SDS-PAGE results showed that the platelet suspension was free of residual proteins and anti-Alb polyclonal antibodies completely inhibited platelet adhesion to adsorbed Alb, but had negligible effect on adsorbed Fg (used as a control); thus confirming that the platelets were adhering to adsorbed Alb and not some other residual protein in the system. Addition of an RGDS peptide to the platelet suspension strongly inhibited platelet adhesion to adsorbed Alb (~60% reduction on CH_3 SAM; $p < 0.01$), while the addition of RGES peptide had no inhibitory effect. Neutralization of arginine residues in the adsorbed Alb layer using 2,3-butanedione reduced platelet adhesion to a similar degree as exposing the platelets to the RGDS peptide in solution. These results indicate that the adhesion of nonactivated platelets to adsorbed Alb is primarily mediated by RGD-specific receptors and the degree to which the binding domains in adsorbed Alb are exposed and/or formed is directly proportional to the degree of adsorption-induced unfolding of the protein. Further studies will be carried out to identify the specific platelet receptors and Alb domains that mediate adhesion. These results indicate that we have much yet to learn about the mechanisms that influence platelet adhesion to adsorbed proteins.

1. Hylton et al, *J. Biomed. Mater. Res.* 73A, 349 (2005).

2. Rodrigues et al, *Biomaterials* 27, 5357 (2006).

3. Sivaraman et al, *Langmuir* 25, 3050 (2009).

Graphene Topical Conference
Room: C3 - Session GR+SS-MoA

Epitaxial Graphene on SiC
Moderator: P.N. First, Georgia Institute of Technology

2:00pm **GR+SS-MoA1 Observing the Quantization of Zero Mass Carriers in Epitaxial Graphene**, ***J.A. Stroscio***, National Institute of Standards and Technology **INVITED**

The cyclotron motion of electrons in a magnetic field has historically been a powerful probe of the Fermi surface properties of metals and two-dimensional electron systems. Oscillations in many measurable properties such as magnetization, thermal conductivity, and resistance, all reflect the quantization of closed orbits and the resulting discrete density of states due to the formation of Landau levels. Here, we show a new ability to observe magneto-oscillations in scanning tunneling spectroscopy of epitaxial graphene as a function of both magnetic field and electron energy [1]. These oscillations arise from Landau quantization of the 2-dimensional Dirac electron and hole quasiparticles in the topmost layer of multilayer epitaxial graphene grown on SiC. In normal metals and two dimensional electron gases the Landau levels are equally spaced. In graphene however, the charge carrier velocity is independent of their energy. Consequently, the Landau level energies are not equally spaced and include a new characteristic zero energy state (the n=0 Landau level). Using scanning tunneling spectroscopy of graphene grown on silicon carbide, we directly observe non-equally spaced energy level spectrum of Landau levels, including the hallmark zero-energy state of graphene. We measure the local variation in the electrostatic potential of graphene by spatially mapping the n=0 Landau level. As the magnetic field is varied at fixed tunneling energy, oscillations are detected in the tunneling conductance, which are shown to be a method to measure low energy electronic band structure. These tunneling magneto-conductance oscillations are used to determine the linear energy-momentum dispersion of graphene through the Dirac point with extremely high energy and momentum resolution.

[1] David L. Miller, Kevin D. Kubista, Gregory M. Rutter, Ming Ruan, Walt A. de Heer, Phillip N. First, Joseph A. Stroscio, Science (in press).

2:40pm **GR+SS-MoA3 Graphene Materials Development**, ***G.G. Jernigan***, *J.L. Tedesco, J.G. Tischler, E. Glaser, J. Caldwell, P.M. Campbell, D.K. Gaskill,* US Naval Research Laboratory, *J.A. Robinson, M.A. Fanton*, Electro-Optics Center Penn State

Development of graphene is a materials issue. Exfoliated graphene has shown the promise of high carrier mobilities, but for graphene to become technologically viable, epitaxial graphene formed over large areas must be developed. Reported carrier mobilities for epitaxial graphene grown on SiC range from > 250,000 to < 1,000 $cm^2V^{-1}s^{-1}$. Mobility results can vary with measurement method, measurement temperature, and sample size. We will present our results, which encompass the aforementioned range of mobilities, for graphene formed on Si-face and C-face SiC.

Utilizing semi-insulating substrates, we have been able to correlate electrical characteristics with materials properties, which are dependent on the surface termination of SiC. Si-face graphene consistently shows lower mobilities than graphene grown on the C-face. XPS shows the differences between growth on the Si-face and the C-face are 1) the presence of an interfacial layer between the graphene and the SiC for Si-face films and 2) electronic differences between the C 1s peak for graphene on the C-face and the C 1s peak for graphene on the Si-face. The electronic differences may result from more graphene layers form on the C-face than on the Si-face. In particular, graphene forms only 1 to 3 layers on the Si-face even for long growth times at high temperature (e.g. 60 min at 1600 °C). STM images of graphene on the Si-face show an islanding mode of growth, which leads to the development of grain boundaries within the film, and μ-Raman measurements show that the mobility increases as the domain size increases. Graphene formed on the C-face of SiC grows very rapidly, leading to films which are 10 to 30 nm thick and decorated with striped surface features (referred to as "giraffe stripes"). Independent of the presence of giraffe stripes, we observe that surface roughness does affect mobility, with smoother surfaces having higher mobilities. We have also performed far infrared magneto-transmission measurements (FIR-MT) on the graphene films. The C-face graphene shows a 0(-1) → 1(0) Landau level transition with a $\sqrt{B}$ dependence and linewidths consistent with layers having carriers described as Dirac fermions with mobilities > 250,000 $cm^2V^{-1}s^{-1}$ at 4.2K. The Si-face graphene showed much broader linewidths resulting from lower carrier mobility. One trend that holds for graphene on both faces of SiC is that fabrication of small area devices can result in higher carrier mobilities and that carrier mobility increases as the carrier density decreases. Continued improvements in the electrical characteristics of epitaxial graphene can be realized through improvements in material quality.

3:00pm **GR+SS-MoA4 Defects Scattering in Graphene**, ***J.-H. Chen***, *W Cullen, C. Jang, M. Fuhrer, E. Williams*, University of Maryland, College Park

We have measured the effect of low energy charged particle irradiation on the electronic transport properties of clean graphene devices. Irradiation of graphene by 500 eV Ne and He ions creates defects that cause intervalley scattering as evident from a significant Raman *D* band intensity. The defect scattering gives a conductivity proportional to charge carrier density, with mobility decreasing as the inverse of the ion dose. The mobility decrease is four times larger than for a similar concentration of singly charged impurities. The minimum conductivity decreases proportional to the mobility to values lower than $4e^2/\pi h$, the minimum theoretical value for graphene free of intervalley scattering. Defected graphene shows a diverging resistivity at low temperature, indicating insulating behavior. The results are best explained by ion-induced formation of lattice defects that result in mid-gap states.

3:40pm **GR+SS-MoA6 Formation of Epitaxial Graphene on SiC{0001}: Comparison of Si-face and C-face**, ***P. Fisher***, IBM, *L. Luxmi, N. Srivastava, R. Feenstra,* Carnegie Mellon University, *Y. Sun,* Argonne National Laboratory, *J. Kedzierski*, MIT Lincoln Laboratory

The formation of epitaxial graphene on the SiC{0001} surface is described, comparing results for (0001) and () surfaces (the so-called *Si-face* and *C-face*, respectively). The graphene is formed by heating the SiC to 1100 – 1400°C for 20 min in vacuum, during which time the Si preferentially sublimates, leaving behind the C which self-assembles into graphene. Development of the graphene layer(s) is observed by atomic force microscopy (AFM), low-energy electron diffraction and Raman spectroscopy, with the graphene thickness measured using both Auger electron spectroscopy and low-energy electron microscopy. High quality films are formed, with field-effect mobilities at room temperature exceeding 4000 cm2/Vs. It is found that graphene forms as 3-dimensional islands on the C-face, whereas it forms in a 2-dimensional manner on the Si-face. We believe that this difference occurs because of differing interface structures between the graphene and the SiC in the two cases. Importantly, the graphene for the C-face is found to be *thinner* in the areas on top of the islands, consistent with a model in which sublimating Si atoms originate from the interface (and hence thicker graphene implies more material loss). For the Si-face a number of morphological features are found to interrupt the flat, uniform morphology of the graphene, including: surface pits, step bunches, and an apparent "secondary" graphitic surface phase. This secondary phase is observed as locally rough regions in the surface morphology. At low graphene formation temperature these regions can extend substantially over the entire surface, but at higher formation temperatures the regions shrink in size, until they produce only a faint finger-like pattern in the morphology as seen by AFM. We tentatively interpret the secondary phase as arising from excess carbon present *on top* of the surface (as opposed to at the graphene/SiC *interface*, where it would form well-ordered graphene).

4:00pm **GR+SS-MoA7 Nucleation of Epitaxial Graphene on SiC(0001)**, ***J.A. Robinson***, *D. Snyder, R. Cavalero, K. Trumbull, M. Wetherington, E. Frantz, M. LaBella, Z. Hughes, M.A. Fanton*, The Pennsylvania State University Electro-Optics Center

Currently, the most promising route for large area graphene, suitable for standard device fabrication techniques, is the sublimation of silicon from silicon carbide (SiC) at elevated temperatures (>1200 °C). Prior to graphene synthesis, SiC substrates are generally hydrogen etched at elevated temperatures to remove residual polishing damage. However, this process can result in significant step bunching, and lead to large terrace step heights. We utilize various surface preparation conditions, Raman spectroscopy, and atomic force microscopy to investigate the nucleation and growth of epitaxial graphene on SiC(0001). The location of graphene was identified using a WITec confocal Raman microscope (CRM) with a 488 nm laser wavelength, diffraction limited lateral resolution of ~ 340 nm, and spectral resolution of 0.24 cm^{-1}. The physical topography of the SiC substrate and graphene films were determined by atomic force microscopy using a Digital Instruments Nanoscope 3A.

We provide evidence that graphene not only nucleates at terrace step edges in the SiC surface, but also at surface defects such as residual surface damage from chemomechanical polishing, and screw dislocations. Prior to graphene synthesis samples were prepared in four manners: 1) *in situ* hydrogen (H_2) etching; 2) *ex situ* potassium hydroxide (KOH) etching; 3) *ex situ* KOH and *in situ* H_2 etching; 4) No etch. Potassium hydroxide selectively etches defect sites on the SiC surface, leaving behind etch pits which serve as macro-defects in the SiC surface. Our monolayer epitaxial graphene was synthesized via Si-sublimation from the Si-face of semi-insulating SiC at 1325°C, 1x10^{-6} Torr. These conditions preclude the formation of graphene on SiC(0001) except at terrace step edges and other topological defects, effectively decorating the nucleation sites for subsequent characterization.

Samples with an *in situ* H_2 etch exhibit growth of graphene nearly exclusively at terrace step edges, while KOH etched samples exhibit graphene synthesis primarily at the etch pits and terrace step edges in the SiC surface. Those samples that experience no pre-treatment exhibit the highest surface coverage of any surface preparation, indicating that graphene grown on SiC(0001) nucleates at atomic scale defects on the SiC surface. This work provides evidence that defects in the form of dislocations, terrace step edges, and etch pits act as low energy nucleation sites for the growth of epitaxial graphene on SiC(0001). Finally, this work suggests that the growth of uniform graphene on SiC(0001) will be heavily influenced by the SiC substrate quality.

4:20pm **GR+SS-MoA8 The Effect of Adsorbates on the Electronic Properties of Graphene***,* ***E. Rotenberg***, Lawrence Berkeley National Laboratory **INVITED**

Epitaxially grown graphene films with various adsorbates have been prepared and investigated using angle-resolved photoemission spectroscopy (ARPES). Two regimes have been studied, which are differentiated by whether the adsorbates preserve the local symmetry of the graphene unit cell or not. For symmetry-preserving defects, such as adsorbed K or Ca atoms, the charge carriers in the graphene retain their metallic, Fermi liquid character, i.e. they can be described as single, weakly interacting "quasiparticles" with a relatively long lifetime as their energy approaches the Fermi level. (This is in contrast to strongly correlated systems where electron-electron scattering dominates the low energy dynamics) In such samples, ARPES measurements of the valence band can determine details of many-body interactions such as electron-phonon coupling. The second regime is followed by adsorbed atomic H atoms, which break the local lattice symmetry, and, for sufficiently high density, cause a dramatic breakdown in the quasiparticle picture, as evidenced by changes to the valence band spectrum. This, together with an accompanying metal-to-insulator transition, suggests that atomic H localizes the carriers, as described by Anderson's theory.

*in collaboration with A. Bostwick, J. L. McChesney, T. Ohta, [LBNL], S. D. Kevan,[U. Oregon] K. V. Emtsev, Th. Seyller [U. Erlangen], and K. Horn [Fritz-Haber Institute]

5:00pm **GR+SS-MoA10 Low Temperature Halogen Assisted Synthesis of Epitaxial Graphene on SiC**, ***M.A. Fanton****, J.A. Robinson, B.E. Weiland, M. LaBella, K. Trumbull*, Penn State University

Graphene presents a host of remarkable physical and chemical properties that are uniquely beneficial for the development of nano-scale electronics and chemical sensors. However, high processing temperatures, and the resulting non-uniform surface topography significantly degrades the electronic properties of epitaxial graphene (EG). To minimize these issues a low temperature, atmospheric pressure, synthesis technique was developed that uses halogen species to extract Si from the SiC surface. This significantly minimizes surface roughening, and reduces substrate-induced strain in the graphene layer, which are major factors limiting material and device performance. The synthesis temperature of epitaxial graphene can be reduced to well below 1400°C by exposing the SiC substrate to halogenated (Cl, Br, F) gases. Our preliminary thermodynamic modeling shows that the formation of carbon on the surface of SiC can be accomplished using various halogen-hydrogen gas mixtures. The model shows that carbon formation on the SiC surface can be controlled using a combination of temperature, pressure, and halogen/hydrogen ratio. Using this technique, both the Si-face and C-face of 2" diameter SiC wafers have been graphitized at temperatures as low as 1150°C at a pressure of 600 Torr. Synthesis was accomplished in a SiC CVD reactor from Structured Materials. Temperatures ranged from 1150°C to 1350°C, making the process compatible with Si-based substrates. Growth pressures ranging from 0.1 to 600 Torr were explored, with higher pressures being preferred. The process atmosphere consisted of a mixture of hydrogen, argon, and halogenated gases such as HCl. The formation and structural quality of the epitaxial graphene was characterized using Raman spectroscopy, atomic force microscopy, transmission electron microscopy, and white light interferometry. Structural quality, as assessed by the Raman G' and D+G peaks, was found to improve as the growth rate decreased and growth temperature increased. Growth rate at a fixed temperature and pressure was readily controlled via the halogen concentration and the halogen/hydrogen ratio as expected from the thermodynamic model. For thick carbon films the growth rate on the C-face was typically 5 times higher than the growth rate on the Si-face. The impact of the halogen/hydrogen ratio was heavily dependent upon the source of the halogen species, which was also expected from thermodynamics. Transmission electron microscopy showed that the interface between the SiC and graphene was sharp and confirmed the number of layers present that was estimated by Raman spectroscopy. The surface roughness of graphene layers was on the order of 1-3nm.

5:20pm **GR+SS-MoA11 Galvanic Deposition of Au Nanoclusters on Epitaxial Graphene***,* ***M. Cerruti****, N. Ferralis, R. Maboudian, C. Carraro*, UC Berkeley

Metallization of graphene surfaces are of crucial importance for the fabrication of metal-graphene contacts, and for surface functionalization via metallic nanostructures. In this paper, a novel method of selective deposition of Au clusters on graphene layers grown epitaxially on SiC substrate is presented. The size and the distribution of particles is regulated and fully controlled by the deposition process. From a combined use of scanning electron microscopy, x-ray electron spectroscopy and Raman microscopy, we propose that cluster nucleation takes place at the edges and defects in graphene domains, via oxidation of defects sites. The preferred nucleation indicates that a high level of selectivity is achieved by controlling the quality of the graphene film.

Nanometer-scale Science and Technology
Room: L - Session NS+BI-MoA

Nanowires and Nanoparticles II
Moderator: L. Bartels, University of California at Riverside

2:00pm **NS+BI-MoA1 Shape Control and Assembly of Colloidal Metal Nanocrystals**, *P. Yang,* University of California - Berkeley*,* ***Henzie***, University of California, Berkeley **INVITED**

Colloidal metal nanoparticles are emerging as key materials for catalysis, plasmonics, sensing, and spectroscopy. Within these applications, control of nanoparticle shape lends increasing functionality and selectivity. Shape-controlled nanocrystals possess well-defined surfaces and morphologies because their nucleation and growth are controlled at the atomic level. An overall picture of shaped metal nanoparticles will be presented, with a particular focus on solution-based syntheses and assembly for the noble metals. General strategies for synthetic control will be discussed, emphasizing key factors that result in anisotropic, nonspherical growth such as crystallographically selective adsorbates and seeding processes. The application of such nanoparticles and their arrays in SERS will be discussed.

2:40pm **NS+BI-MoA3 Properties of InP/InAs/InP Core-Shell Nanopillars Grown by Metalorganic Vapor-Phase Epitaxy***,* ***V. Evoen****, L. Gao, S. Chowdhury, R. Woo, B. Liang, M. Pozuelo, S. Prikhodko, M. Jackson,* University of California, Los Angeles*, N. Goel, M. Hudait,* Intel Corporation*, D. Huffaker, M. Goorsky, S. Kodambaka, R. Hicks*, University of California, Los Angeles

Compound semiconductor nanowire devices are of great interest due to their size-dependent electrical and optical properties and their potential applications in nano-electronics. In this study, we demonstrate the growth of InP/InAs/InP core-shell nanopillars by metalorganic vapor-phase epitaxy (MOVPE). Indium droplets were used to catalyze crystal nucleation at low temperature. At 400°C and a V/III ratio of 86, hexagonal pillars were grown with smooth side walls and average widths and heights of 45 and 70 nm, respectively. Scanning and transmission electron microscopy, electron backscattered diffraction, and selected area electron diffraction revealed that the pillars were single crystal wurtzite and were bounded by {1,-1,0,0} sidewalls. Indium arsenide quantum wells were deposited on the nanopillars at 395°C and a V/III ratio of 120, and then capped with a thin layer of InP. The thickness of the quantum well was ~5 nm. Photoluminescence spectra at 77 K yielded a single intense band at 1750 nm (0.7 eV) with a full width at half maximum of 350 nm. These results indicated that there was phosphorus and arsenic intermixing with formation of an InAsxP1-x alloy. Further growth experiments varying temperature, V/III ratio, and hydrogen interrupt time succeeded in shifting the photoluminescence peak closer to the band gap for InAs. Detailed measurements of the optical and electrical properties of the core-shell nanopillars will be presented at the conference.

3:00pm **NS+BI-MoA4 Synthesis of Vertically Aligned and Patterned Silicon-Carbon Core Shell Nanotubes**, ***J. Song***, *R. Vanfleet, R.C. Davis*, Brigham Young University

Here we report the first synthesis of silicon-carbon core-shell nanotubes (SiCNTs). The SiCNTs are formed by coating a vertically aligned and patterned carbon nanotube(CNT) forest with low pressure chemical vapor deposition (LPCVD) of silicon. The carbon nanotube forests were grown from a patterned thin film Fe catalyst resulting in high aspect ratio three dimensional microscale structures up to 500 microns tall with vertical sidewalls. The density of the nanotubes in the forests is very low; the nanotubes fill only about 1 percent of the space by volume. Silicon LPCVD layers (~30 nm thickness) are deposited conformally, coating the nanotubes and significantly increasing the mechanical strength of the structure. By adjusting the silicon deposition temperature, amorphous or crystalline silicon shells can be formed. This combination of silicon LPCVD on VACNTs yields a unique fabrication approach resulting in porous three dimensional silicon structures with precise control over shape and porosity.

3:40pm **NS+BI-MoA6 Structure and Electron Transport through Molecules Assembled in Multi-Component Molecular Gradient Layers**, ***N. Ballav***, *P. Morf,* Paul Scherrer Institute, Switzerland, *F. Nolting,* Swiss Light Source, Switzerland, *F. Wrochem, H.-G. Nothofer, A. Yasuda, J. Wessels,* Sony Deutschland GmbH, Germany, *T.A. Jung*, Paul Scherrer Institute, Switzerland

Surface molecular gradients are essential for the fast screening of molecular and cellular adhesion and motion in assays and have been used to relate molecular binding with the biological response for functional biomolecular entities. They are being used for optimizing the properties of bio-interfaces, bio-chips, bio-assays, and bio sensors, and for controlling wettability to induce movement in water droplets. Herein we present a new method to fabricate self-assembled monolayer (SAM) based multi-component molecular gradients comprising constituents with specific head or tail groups attached to different molecular backbones. We demonstrate for the first time how local (STM) and non-local (NEXAFS) methods can be combined with theoretical calculations (DFT) to draw conclusions on structure, orientation and local processes, in particular electronic conductance in the gradient layer (1). Our achievement goes beyond previous works in the ability to visualize molecular gradient layers and to study the anisotropy of physicochemical properties with laterally changing composition.

4:00pm **NS+BI-MoA7 Reduction, Morphology, and Conductivity of Pd Nanoparticles on Pyridine-Terminated Self-Assembled Monolayers**, ***C. Silien***, University of Limerick, Ireland, *M. Buck, S. Francis, M. Caffio, B. Wang, R. Schaub,* University of St Andrews, UK, *D. Lahaye, N.R. Champness*, University of Nottingham, UK

Metallization of organic self-assembled monolayers (SAMs) is generally impeded by the penetration of metal through the film. A two-step scheme, involving coordination of metal ions and electrochemical reduction in separate solutions [1], was recently proposed to circumvent the problem, opening up new opportunities for the preparation of low-dimensional metal structures on SAMs. This strategy was further investigated using SAMs of newly designed pyridine-terminated molecules (ω-(4-pyridine-4-yl-phenyl)-alkanethiol, PyPn, with n=2,3) [2], which combine the high structural integrity and quality of biphenyl-based SAMs [3,4] with the chemical functionality afforded by the pyridine moiety. Pd adlayers on PyPn SAMs on Au(111) were prepared by reduction of Pd^{2+} either directly from solution or following the two-step scheme [1]. Scanning tunneling microscopy (STM) revealed that, in both cases, and independently of the alkane spacer length, Pd systematically organizes into nanoparticles that are weakly bonded onto the pyridine moieties (*i.e.*, easily displaced with tunnel current of the order of a few pA), exhibit a narrow height distribution around 2.4 nm and display a Coulomb gap of ~ ±0.20 V. These data strongly suggest that the Pd nanoparticles are not contacted with the Au substrate. Moreover, the nanoparticle coverage can be increased up to a monolayer, revealing that it is more favorable to generate new nanoparticles than to add material to existing ones. It is proposed that Pd^{2+} reduction is not mediated by structural defects in the SAM. Lateral diffusion of Pd adatoms and nanoparticles occurs on the SAM and explains the morphology of the Pd adlayer.

[1] Baunach, T.; Ivanova, V.; Kolb, D. M.; Boyen, H.-G.; Ziemann, H.-G.; Büttner, M.; Oelhafen, P. *Adv. Mater.* **2004**, *16*, 2024-2028.

[2] Silien, C.; Buck, M.; Goretzki, G.; Lahaye, D.; Champness, N. R.; Weidner, T.; Zharnikov, M. *Langmuir* **2009**, *25*, 959-967.

[3] Cyganik, P.; Buck, M.; Wilton-Ely, J. D. E. T.; Wöll, C. *J. Phys. Chem. B* **2005**, *109*, 10902–10908.

[4] Cyganik, P.; Buck, M.; Strunskus, T.; Shaporenko, A.; Witte, G.; Zharnikov, M.; Wöll, C. *J. Phys. Chem. C* **2007**, *111*, 16909–16919.

4:20pm **NS+BI-MoA8 Estimation of Thermal Conductivity of Si and Oxide-Covered-Si Nanowires by Molecular Dynamics Simulation**, ***T. Saegusa***, *K. Eriguchi, K. Ono,* Kyoto University, Japan, *H. Ohta*, University of California, Santa Barbara

Nanowires (NWs) have attracted much attention because they are expected to be applicable to various devices such as the field-effect transistors, solar cells, and thermoelectric devices. The reason is that in nanostructures, we can see some peculiar phenomena which are not observed in bulk materials. One of the phenomena is the lower thermal conductivity of NWs [1]. The thermal conductivity of NWs is one to two orders of magnitude lower than the bulk value (~168 W/mK at 300K). This is appreciated to occur by confinement of the phonon propagation. The phonons are prevented by surface scattering due to the small wire radius. This means that surface atoms may have a great influence on material properties. Experimental observations of the thermal conductivity by P. Yang's group [1] as well as theoretical studies by different approaches such as Boltzmann transport equation, Monte Carlo (MC) method for phonon propagation [2], and molecular dynamics (MD) simulations [3] have been published. In addition, Hochbaum *et al.* experimentally observed the reduction of thermal conductivities in Si-NWs fabricated by electroless etching, where silicon NWs were coated by native oxides [4]. These studies indicate thermal conductivities are very sensitive to surface structures.

In this paper, we present the thermal conductivity of naked Si-NWs and oxide-coated Si-NWs at 300 K, evaluated by employing direct nonequilibrium MD simulation with the Stillinger-Weber interatomic potential model for Si/O systems. The thermal conductivity was obtained for various cross sections (2-8 nm^2) and lattice orientations (<100>, <111>, and <110>). The thermal conductivity for naked Si-NWs with cross sections of 2-8 nm^2 at 300 K was 2-10 W/mK, which was in good agreement with that for <100>Si-NWs (1-2 W/mK) obtained from equilibrium MD simulation by Volz *et al*. [3] and from MC simulation by Chen *et al*. [2]. We found the small dependency of thermal conductivity on the lattice orientation. In case of oxide-coated Si-NWs, the thermal conductivity was reduced as the thickness of Si-oxides increased. To check our simulation results, we also analyzed the strain in Si-NW due to surface oxidized layers. Detailed simulation results and analytical approach for various surface structures or cross-sections will be shown at the conference.

[1] D. Li *et al*., Appl. Phys. Lett. **83**, 2934(2003)

[2] Y. Chen *et al*., Journal of Heat Transfer, Transaction of ASME, **127**, 1129(2005)

[3] S.G.Volz *et al*., Appl. Phys. Lett. **75**, 2056(1999)

[4] A.I.Hochbaum *et al*., Nature, **451**, 163(2008)

4:40pm **NS+BI-MoA9 Temperature Dependence of Carbon Nanofiber Resistance**, ***H. Yabutani***, *T. Yamada, T. Saito, C. Yang*, Santa Clara University

To assess their potential for interconnect applications, the interplay between electrical and thermal transport in carbon nanofibers (CNFs) under high-current stress is examined. Current-voltage measurement results obtained during each stress cycle reveal temperature-dependent behavior of CNF resistance, the analysis of which is the subject of this paper.

To minimize the contact resistance between gold electrode and CNF, tungsten is deposited on each electrode using focused ion beam [1]. For each test device, we apply stressing current progressively, *i.e*., in the first cycle, a small current is applied for three minutes, and in the second cycle, a slightly larger current is applied for another three minutes, etc. Using this scheme, we obtained a decrease in average resistance with increasing stressing current for each stress cycle. In ref. [2], we presented a heat transport model that takes into account Joule heat generation, dissipation, and diffusion during current stressing. In this model, the CNF temperature along its length was determined as a function of stressing current. Since the increase in temperature originates from Joule heating, and since we established that current stressing has little effect on the total resistance at ambient temperature prior to breakdown [1], this result suggests that the reversible resistance change due to Joule heating is a result of change in bulk CNF properties at elevated temperatures.

The mechanism for CNF bulk resistance decrease with temperature was discussed in the context of transport in disordered media [3]. Our CNF devices have impurities and/or lattice defects, which often serve to trap carriers. Thermal energy releases these carriers from the trap centers, giving rise to lower resistance. Thus transport is controlled by thermal activation of these trapped carriers and their subsequent re-trapping as the temperature is lowered. The same mechanism would account for the observed decrease in resistance as the temperature increases with increasing stressing current due to Joule heating.

[1] T. Saito, T. Yamada, D. Fabris, H. Kitsuki, P. Wilhite, M. Suzuki, and C. Y. Yang, *Appl. Phys. Lett.* **93**, 102108 (2008).

[2] T. Yamada, T. Saito, D. Fabris, and C. Y. Yang, *IEEE Electron Device Lett.* **30**, 469-471 (2009).

[3] Q. Ngo, T. Yamada, M. Suzuki, Y. Ominami, A. M. Cassell, J. Li, M. Meyyappan, and C.Y. Yang, *IEEE Transactions on Nanotechnology* **6**, 688-695 (2007).

5:00pm **NS+BI-MoA10 Relative Stability of Aromatic Self-Assembled Monolayers Formed by Thiols and Selenols**, ***K. Szelagowska-Kunstman***, *P. Cyganik,* Jagiellonian University, Poland, *B. Schüpbach, A. Terfort*, Goethe-Universität Frankfurt, Germany

Aromatic self-assembled monolayers (SAMs) are considered a model system for molecular electronics applications.[1] However, potential use of these monolayers in real devices is limited by significant concentration of structural defects,[2] which disturb functions of the metal-molecule-metal junction. One of strategies we propose to optimize structure of aromatic SAM's is selection of proper headgroup atom binding SAMs to the substrate.[3,4]

In this presentation we report on stability of two analogous aromatic SAMs bound to the Au(111) substrate by S or Se atom. To compare stability of both systems we analyze exchange of molecules constituting complete SAM monolayer during incubation in solution containing other aliphatic thiol or aliphatic selenol molecules.[5] The exchange experiments have been performed by comparing not just a single SAM but two entire homologue series of BPnS (CH_3-$(C_6H_4)_2$-$(CH_2)_n$-S-, n = 2-6) and BPnSe (CH_3-$(C_6H_4)_2$-$(CH_2)_n$-Se-, n =2-6) molecules on Au(111) surface. Quantitative control of the exchange process was obtained using Infrared Reflection Adsorption Spectroscopy. These data will be discussed together with our recent microscopic study which found that binding by selenium atoms improve significantly the ordering of these SAMs and influences molecule-substrate interaction.[4] Obtained results clearly indicate higher stability of SAMs based on selenols in comparison to their thiol analogs.

References

[1] C. Love , G. et al. **2005**, *Chem. Rev.*, *105*, 1103.

[2] D. Käfer et al.. **2006** *J. Am.Chem. Soc. 128*, 1723.

[3] A. Shaporenko, et al. **2005** *J. Phys. Chem. B 109*, 13630.

[4] P. Cyganik et al. **2008** *J. Phys. Chem. C 112,* 15466.

[5] K. Szelagowska-Kunstman, P. Cyganik, B Schüpbach, A. Terfort **2009** *in preparation*

Plasma Science and Technology
Room: A1 - Session PS+MS-MoA

Plasma Challenges at the 22nm Node and Beyond
Moderator: C. Labelle, GLOBALFOUNDRIES

2:00pm **PS+MS-MoA1 Plasma Etch Challenges for 22nm Advanced Logic Development**, ***R. Wise***, IBM **INVITED**

At the 22nm technology node for logic devices many novel semiconductor technologies are being considered, each of which impacts etch process development and control. These technology performance challenges drive increases in carrier mobility (necessitating application of high strain liner and epi materials and reduction in silicon loss budget and gate height scaling), increased packing density (limiting resist trim budgets, increasing CD shrink requirements, and increasing integration of eDRAM), and achieving target resistance and capacitance (necessitating the introduction of porous low-k dielectrics and better profile control). The challenges introduced by these elements on dry etch processes, tooling, and controls is discussed in detail.

Widespread aggressive device scaling beyond lithographic limits require dry etch processes to provide controllable CD reduction to meet design groundrules. In particular, limited improvement in imaging at the 22nm node results in challenges in scaling on the plasma equipment. The implementation of multiple exposure techniques to achieve design rules for several key levels drives additional process control across multiple exposure and etch steps. Reduction in the available mask thickness required to preserve the lithography process window have driven the need for highly selective etch processes, generally at the expense of uniformity, defectivity, and profile of the transferred pattern. Later generation lithographic materials are expected to continue to exhibit increased sensitivity to line edge roughness, and drive additional implementation of novel masking materials. Process and tooling technology needs required to address these imaging challenges are discussed.

2:40pm **PS+MS-MoA3 22nm Technology Manufacturing Challenges - Window for Process Control becomes Smaller and Smaller, Equipment and Material Interaction Becomes Unpredictable and Manufacturing Costs Increase**, ***P. Adam***, GLOBALFOUNDRIES Dresden, Germany **INVITED**

Increasing complexity and smaller and smaller CD for 22 nm technologies will have also a major impact for all plasma supported processes. The limited understanding of plasma and device interaction in existing technologies will further challenge the equipment suppliers to develop solutions for high volume manufacturing fabs. Some examples will be shown to illustrate this statement. Fab Engineers will see unexpected behaviour of materials in process chambers and surprising results of their plasma process on the device itself. A big amount of this will not be seen in the application labs of the equipment suppliers. Part of the problem is availability of appropriate test wafer material which can reflect the final manufacturing situation sufficient enough. Designs from different companies will behave most likely also differently. Therefore equipment suppliers have to move their development process close into the manufacturing site of the fabs. On the other side, semiconductor fab would like to get a tool and a process ready to go. They don't have the time and the manpower to support this kind of development work for the equipment supplier. All this will drive additional cost for both supplier and costumer.

How we can overcome this situation? Some ideas will be presented highlighting the complexity of the situation and the need for close interaction of all involved parties.

3:40pm **PS+MS-MoA6 Logic Etch Challenges at the 22nm Node and Beyond**, ***V. Vahedi***, *G. Kamarthy, J. Guha, H. Singh*, Lam Research Corporation **INVITED**

Due to increased device integration complexity, there are significant challenges to technology scaling for Logic devices at 22nm and beyond. The issues range from difficulties in scaling device threshold voltage (V_t), and electron and ion mobility enhancements to achieving the proper leakage current for low power devices. Proposed solutions to overcome these challenges include adoption of Metal Gate High-k for threshold voltage and leakage current engineering, to various Strained Silicon techniques to enhance electron and ion mobility, and FinFETs for beyond 22nm technology node. In this presentation, we will review some of challenges associated with front-end logic integration schemes, such as control of Si Recess and Si damage. Si loss and damage after gate etch, spacer etch, and strained Si etch applications can impact source-drain junction depth, and increase device leakage. We will discuss various mechanisms for Si loss and damage, work done by previous authors, what is required at 22nm and beyond, implication for etch and post etch clean, and areas where better understanding is required.

Advanced Surface Engineering
Room: C4 - Session SE-MoA

Atmospheric Pressure Plasmas
Moderator: M.S. Wong, National Dong Hwa University, Taiwan

2:00pm **SE-MoA1 Production-scale Processing of Flexible Substrates using High Power, Low Temperature, Atmospheric Pressure Plasma Technology**, ***G.S. Selwyn***, APJeT, Inc. **INVITED**

The application of vacuum-based plasmas in semiconductor processing has helped lead the microelectronics revolution and today is a highly-developed and mature technology. However, the high cost of operation and maintenance for vacuum-based plasma, along with the limitation for treating vacuum-compatible substrates, greatly limits future applications using this technology. In contrast to the vast expansion of vacuum-based plasma over the last 30 years, non-equilibrium, atmospheric-pressure plasma has a 125 year history dating back to Siemen's original invention of the dielectric barrier discharge. Yet, the applications for atmospheric pressure plasma industry represent only a tiny fraction of today's use of vacuum-based plasma. Part of the reason for this is the low power density that Dr. Siemen's atmospheric pressure plasma was able to achieve and the faster processing rates and improved control vacuum-based plasma was able to provide. This talk will review and compare the various kinds of atmospheric pressure plasma sources and will illustrate the use of a high-power, stable, non-equilibrium atmospheric pressure plasma that operates with a gas temperature below 30C for low-cost processing of commodity materials, such as textiles, non-wovens and plastic films. A full-scale production machine that uses 72" electrodes and which operates at 10KW will be shown, along with the unique process this technology enables.

2:40pm **SE-MoA3 Effect of the Electrode Material in the Atmospheric Plasma Abatement of NO from Air Mixtures**, ***L. Bardos***, *H. Barankova*, Uppsala University, Sweden

Protection of the environment requires more stringent limits on engine exhausts, power plant emissions and all other sources of air pollution. Different air cleaning technologies are being developed and applied for removal of pollutant gases like NO, NO2, SO2 and CO2. A very promising treatment is based on non-thermal (cold) plasmas at atmospheric pressure where dominant energy carriers are electrons and the dominant chemistry is based on formation and interactions of gaseous radicals. A widely supported method of cleaning air mixtures in the exhausts of diesels and combustion plants from NO and NO2 utilizes the Plasma Assisted Catalytic Reduction where the cold plasma is combined with the solid-state catalyst. In this method the plasma acts as an oxidation catalyst where an atomic oxygen from air oxidizes NO to NO2 and the solid-state catalysts are then capable to convert all NO2 to N2 and O2. However, in most cases it is necessary to involve also auxiliary gases, typically hydrocarbons (propene, ammonia), to make the process efficient. The present work introduces an original cold plasma system based on atmospheric hollow cathodes working in a pulsed dc regime with variable pulse voltage and repetition frequency. The system design and parameters have been optimized for the best conversion performance. It has been found that the material of electrodes can affect the oxidation efficiency of the plasma substantially. The graphite electrodes allowed the 100% conversion of NO to NO2 without any auxiliary gas. Effects of several materials on the conversion efficiency are compared and discussed.

3:00pm **SE-MoA4 Mechanism for the Surface Activation of Polymers by Remote Atmospheric Pressure Plasma**, ***E. Gonzalez***, *M. Barankin*, University of California, Los Angeles, *P. Guschl*, Surfx Technologies, LLC, *R. Hicks*, University of California, Los Angeles

An atmospheric pressure oxygen and helium plasma was used to activate the surfaces of polyethylene (PE) and polymethyl methacrylate (PMMA). The plasma physics and chemistry was investigated by numerical modeling. It was shown that as the electron density of the plasma increased from $3x10^{10}$ to $1x10^{12}$ cm^{-3}, the concentration of O atoms and metastable oxygen ($^1\Delta_gO_2$) molecules in the afterglow increased from $6x10^{15}$ to $1x10^{17}$ cm^{-3}, while the concentration of ozone decreased from $5x10^{15}$ to $2x10^{15}$ cm^{-3}. The oxygen atoms, metastable oxygen ($^1\Delta_g$ O_2) molecules and ozone were the principle reactive species present in the afterglow. Exposing the polymers to the plasma afterglow for up to 30 seconds led to surface activation and an increase in bond strength of the polymers to adhesives by as much as 16 times. X-ray photoelectron spectroscopy of PMMA revealed an 8% increase in the C 1s peak area attributed to carboxylic acid groups (288.9 eV). In addition, the C 1s peak due to the methyl pendant groups (285.0 eV) decreased by 5%. The O:C ratio of PMMA increased from 0.4 to 0.7 after plasma treatment. Surface analysis of the polymers by internal reflection infrared spectroscopy confirmed the presence of carboxylic acid groups at 1710 cm^{-1} and hydroxyl groups at 3100 to 3500 cm^{-1} after activation. These results indicate that oxygen atoms and metastable O_2 molecules generated in the plasma rapidly oxidize the polymer chains. The experimental results as well as a detailed description of the reaction mechanism will be presented at the meeting.

3:40pm **SE-MoA6 Coating Growth Behavior during the Plasma Electrolytic Oxidation Process**, ***R.O. Hussein***, *D.O. Northwood, X. Nie*, University of Windsor, Canada

In this study, aluminum oxide was deposited on an Al-alloy substrate to produce hard ceramic coatings using a Plasma Electrolytic Oxidation (PEO) process working at atmospheric pressure. Two different operation modes were used, namely a DC power mode and pulsed DC power mode with different frequencies. Optical Emission Spectroscopy (OES) was employed to study the species, electron temperature and densities of the plasma. The morphology, composition, and microstructure of the coatings on the Al substrate were investigated using Scanning Electron Microscopy (SEM) with energy dispersive X-ray (EDX) analysis, and X-ray diffraction. At the early stage of the PEO process the plasma electron temperature increased which shows the same trend as the output voltage. Aluminum emission line intensities (which are related to the spark behavior during the discharge) were higher for the pulsed DC mode than that from DC mode, causing different surface morphologies. It was also found that pulsed DC mode enhanced the coating growth during the early discharge stage, due to the strong ejection of aluminum from the substrate-oxide interface during the plasma discharges. The coating characteristics and OES analysis thus led to a better understanding of the ceramic coating growth behavior as influenced by the power operation modes.

*Corresponding author. Tel: 1-519-253- 3000, ext. 4148; Fax: 1-519-971-7007; E-mail address: xnie@uwindsor.ca (X. Nie)

4:00pm **SE-MoA7 Saddle-like ICP Antenna for RF Atmospheric Plasma Processes**, ***Y. Glukhoy***, American Advanced Ion Beam Inc.

A saddle-like ICP antenna with the several spiral coils distributed with an angular uniformity and enveloping a quartz tube of a plasma reactor was developed. It generates a transversal RF field directed normally to axis of this reactor. Due to such a design property of this antenna can be tuned between an initial capacitively coupled and a following inductively coupled state to facilitate a plasma ignition especialy at atmospheric pressure. Unlike a conventional coil generating a filament-like ICP atmospheric discharge this antenna provides a larger high temperature area for evaporation of precursor as well as for a plasma-chemical reaction. This antenna was successfully tested for nanocoating by silicon dioxide of the different surfaces including the inner walls of the hollow articles.

1. Y.Glukhoy, I. Ivanov RF Atmospheric Plasma Systems for Nanopowder Production and Deposition of Nanocrystallines. AVS 53rd International Symposium, San Francisco, California, November , 2006 CA, USA.

4:20pm **SE-MoA8 Diagnostic Study of an Arc Plasma Jet Under Atmospheric Pressure and Its Applications to Materials Processing**, ***C.C. Hsu***, *C.Y. Wu, Y.W. Hsu, Y. Lin, Y.J. Yang*, National Taiwan University

An atmospheric-pressure arc plasma jet was studied, and its use for material processing will be presented. This plasma jet was sustained by a DC pulsed power source of 20 kHz ~ 40 kHz using nitrogen. A voltage probe and a current probe were used to monitor the voltage and current (I-V) waveforms. The optical emission at the plasma jet downstream was monitored by an optical emission spectrometer. Multiple thermocouples were used to measure the downstream jet temperature. The I-V waveforms reveal that the jet undergoes abnormal glow to arc transition within each pulse power period. This transition is shown to be critical for sustaining a stable plasma jet and is primarily controlled by the power input to the plasma in the abnormal glow regime. Temperature and optical emission measurements show that the jet temperature decreases and the excited-state species densities increase with the increase of the gas flow rate, while both quantities increase with the increase of the applied voltage. These allow for the independent control of the temperature and the excited-state species densities by using these two operating parameters. The use of this plasma jet for materials processing, namely zinc oxide thin-film deposition and niobium oxide nanowire fabrication, will be presented. The correlation between the plasma behavior and the fabricated materials characteristics will be discussed.

Surface Science
Room: M - Session SS1+EM-MoA

Semiconductor Surfaces and Interfaces I: Ge and III-V's
Moderator: M. Losurdo, IMIP-CNR, Italy

2:00pm **SS1+EM-MoA1 III-V MOS Device Performance Enhancement by Detection and Control of Individual Surface Oxidation States**, ***C.L. Hinkle***, *M. Milojevic, A.M. Sonnet, E.M. Vogel, R.M. Wallace*, University of Texas at Dallas **INVITED**

Field effect transistors (FETs) remain at the heart of integrated circuit technology, and are forecasted to do so for at least the next decade. Silicon has been the material of choice for this purpose, but appears to be reaching significant performance limitations with further device dimension shrinking. As a result, the use of alternative semiconductor materials has again become of interest for FE T s. However, the native oxides (As-O and Ga-O) of these materials have been shown for more than thirty years to be of poor quality for metal-oxide-semiconductor (MOS) device performance. Furthermore, deposition of any gate oxide onto a clean III-V surface results in the oxidation of the substrate to detrimental effects. Despite the extensive research of III-V materials, there is still much to be understood about these oxides. In particular, the individual oxidation states of As (5+ and 3+) and Ga (3+ and 1+) are rarely considered despite evidence that they are quite different in forming defect states.

Recent work [1,2,3] will be presented on the detection and control of each of these surface oxidations states through carefully managed interfacial reactions and depositions on GaAs and InGaAs. The fabrication of MOS capacitors and FETs with these studied interfaces has led to a correlation between the spectroscopy and electrical measurements. An emphasis on controlling or eliminating each oxidation state through a variety of techniques has allowed for a detailed understanding of these native oxides and how each one affects device performance. The presence of the Ga 1+ oxidation state is spectroscopically detected for the first time at these interfaces and a dramatic increase in device performance is demonstrated by controlling the Ga 3+ surface concentration. This work is supported by the

FCRP Materials, Structures, and Devices (MSD) Center, SEMATECH, FUSION funded by System IC 2010 (COSAR), The Texas Enterprise Fund, and NIST, Semiconductor Electronics Division.

[1] Hinkle et al., APL **94**, 162101 (2009).

[2] Sonnet et al., APL. **93** 122109 (2008).

[3] Hinkle et al., IEEE EDL **30**, 316 (2009).

2:40pm **SS1+EM-MoA3 Unpinning of $In_xGa_{1-x}As$(001)-(4x2)/*c*(8x2) via Oxide Deposition for III-V MOSFETs**, ***J.B. Clemens***, *S.R. Bishop, A.C. Kummel*, University of California, San Diego

The formation of a semi-ordered oxide passivation layer between hafnium oxide and $In_{0.53}Ga_{0.47}As$(001)-(4x2)/*c*(8x2) and InAs(001)-(4x2)/*c*(8x2) was studied using scanning tunneling microscopy/spectroscopy (STM/STS), and density functional theory (DFT) calculations. A passivation layer is needed to protect the surface from disruption during bulk amorphous oxide deposition for a high-κ gate insulator. Two methods of forming low coverage of HfO_2 were investigated: reactive oxidation of the e-beam deposited Hf metal and e-beam deposition from an HfO_2 target. STM results show that Hf atoms must cluster to be reactive to O_2. DFT suggests there is a high tendency for Hf to displace substrate atoms, which is undesirable. Direct deposition of the oxide is a better method. At submonolayer coverage, STM has identified individual bonding sites for the HfO_2 molecule; the HfO_2 forms small structures of mostly monolayer height with a high nucleation density. Density functional theory (DFT) calculations have been employed to assign the bonding structure. The DFT simulations show that for HfO_2/InAs(001)-(4x2), the most likely sites are stable by about -4.5 eV and the calculated density of states (DOS) shows no evidence of Fermi level pinning (no mid-gap states). At submonolayer coverage, the HfO_2 molecule bonds via group III-oxygen bonds and group V-hafnium bonds. STS measurements of clean InGaAs(001)-(4x2) reveal that the surface has significant band bending, showing p-type character for both n-type and p-type samples. Deposition of > 1 ML of HfO_2 is enough to move the Fermi level towards the conduction band for n-type InGaAs(001)-(4x2), as shown in results of STS vs. HfO_2 coverage. For p-type material, the Fermi level remains near the valence band after deposition of HfO_2. These results are consistent with the Fermi level remaining unpinned. In addition, annealing effects are studied. At temperatures of 300 °C and above, ordered oxide structures are seen in STM which form rows in the [-110] direction. However, lower annealing temperatures of 200 °C and below are preferable for good STS results. Hafnium oxide, evaporated via electron beam deposition, likely creates some O_2 and HfO, which may react in an undesirable way with the semiconductor surface. For this reason, a method is also proposed to protect the surface during e-beam deposition via a CO_2 protecting layer at low temperature (90 K), which does not appear to perturb the surface.

3:00pm **SS1+EM-MoA4 Formation and Structure of Alkaline Earth Template Layers for Oxide Epitaxy on Semiconductor (100) Surfaces**, *B. Lukanov, K. Garrity, J. Reiner, F.J. Walker, C.H. Ahn, S. Ismail-Beigi*, ***E.I. Altman***, Yale University

The finding that alkaline earth titanates can be epitaxially grown on Si and Ge(100) surfaces with atomically abrupt interfaces without oxidizing the semiconductor has spurred research into exploiting these materials for high k gate dielectrics, and for integrating new functionality into semiconductor devices. Attempts to epitaxially grow other oxides with similarly abrupt interfaces have thus far failed. It has been suggested that the initial interfacial layer formed by the reaction between the alkaline earths and Si and Ge is key to the success achieved with the alkaline earth titanates; therefore, we have been studying the interaction Sr and Ba with Ge and Si(100) with scanning tunneling microscopy (STM), complemented by density functional theory (DFT). At elevated temperatures, both Sr and Ba cause massive restructuring, indicative of surface alloy formation. Initial deposition causes an apparent etching away of the substrate dimers leading to dimer chains and islands on the surface. For Sr on Ge(100), increasing the coverage leads to an apparent c(4x4) structure decorated by bright spots that order only locally; the density of these bright spots decreases with increasing Sr coverage. The apparent c(4x4) structure ultimately gives way to a (3x2) structure that is characterized by periodic arrays of islands and trenches when it completely covers the surface. Electron diffraction data shows that continuing to raise the coverage causes a structural transformation to a (2x1) structure. On the atomic scale, STM images of the apparent c(4x4) and (3x2) structures vary dramatically with imaging bias; in particular changing the polarity of the bias voltage causes a contrast reversal where bright features in filled state images appear dim in empty state images and vice versa. Based on the observed bias dependence for Sr adatoms deposited at 300 K and simulated images derived from DFT calculations, a model of the (3x2) structure was developed in which Sr atoms replace every third row of Ge atoms on the surface. The striking periodic island and trench morphology is then associated stress relief of the (3x2) structure. The results clearly show that at elevated temperatures the template layer does not form through simple surface adsorption.

3:40pm **SS1+EM-MoA6 STS and KPFM Investigation of InAs Pinning and Unpinning**, ***W. Melitz***, *J. Shen, S. Lee, A.C. Kummel*, University of California, San Diego

A combined scanning tunneling spectroscopy (STS) and Kelvin probe force microscopy (KPFM) study was performed on InAs(001)-(4×2) to elucidate the surface electronic properties since this surface is a leading candidate for III-V MOSFETs. KPFM provides higher energy resolution than STS, which is critical for studies of materials like InAs which have small band gaps (Eg=0.354 eV). Amplitude modulation (AM) mode KPFM provides especially high energy resolution (10 meV) and is free of tip induced band bending because of the low applied voltage (70 meV). STS spectra of InAs(001)-(4×2) consistently show pinning, with the surface Fermi level near the conduction band for both n-type and p-type samples even on nearly defect free surfaces. Using KPFM, the work functions for both n-type and p-type clean InAs(001)-(4×2) surfaces is 4.3 eV consistent with surface pinning. Using the electron counting rule, indium dimers in the trough are sp^2 hybridized having a completely empty dangling bond. However the indium dimer atoms are positioned in a sp^3 tetrahedral configuration; these strained bonding sites might be responsible for the pinning. If the pinning is solely due to the (4×2) reconstruction, it is expected that other reconstructions without indium dimers would be unpinned. KPFM was also performed on cross-sectional InAs, which is defect free and has no indium dimers. These results were consistent with the bulk values with a work function difference between n-type and p-type of 0.49 eV. By eliminate the buckled indium dimer states with a passivation layer the InAs(001)-(4×2) surface could become unpinned.

4:00pm **SS1+EM-MoA7 Doping of InP Nanowires Studied by STM and X-ray PhotoEmission Electron Microscopy**, ***M. Hjort***, *A.A. Zakharov, M.T. Borgström, E. Hilner, R. Timm, A. Fian, J.N. Andersen, E. Lundgren, L. Samuelson, A. Mikkelsen*, Lund University, Sweden

Self-assembled III-V nanowire heterostructures could be key components in many future optoelectronic devices [1], for example solar cells [2]. To realize photovoltaics from these structures variable p- and n-type doping along the nanowires are a fundamental prerequisite. The active component in solar cells, the pn-junction, has been grown axially in InP nanowires with different p- and n-type doping levels. However determining specific doping levels, effects of the nanowire surfaces and junction abruptness and band alignment across the interface with any precision is very difficult. Recently we have shown that scanning tunneling spectroscopy on nanowires with high resolution is possible [3] and we are now combining this with synchrotron based photoemission methods.

We have examined InP nanowires with up to two axial pn-junctions with Spectroscopic PhotoEmission and Low Energy Electron Microscopy (SPELEEM), X-ray Photoelectron Spectroscopy (XPS) as well as Scanning Tunneling Microscopy/Spectroscopy (STM/S). These techniques have given us the possibility to probe not only the structure of the nanowires but also the electrical properties (such as doping level) with high lateral resolution.

With our different setups we can probe the local density of states, atomic scale structure and work function differences along the wires. We can clearly distinguish between the different n- and p-type parts of the nanowires with both the scanning probe as well as with the synchrotron radiation based techniques. Both surface and the inner regions of the wires can to some extent be probed by varying photon energies in SPELEEM or modifying the surface for STM. This gives us the opportunity to understand the device at many different levels and improve its future quality.

[1]. L. Samuelson et al., *Physica E* **2004**, 21, 560-567

[2]. M. T. Borgström et al., *Nanotechnology* **2008**, 19, 445602

[3]. E. Hilner et al., *Nano Letters* **2008**, 8 (11), 3978-3982

4:20pm **SS1+EM-MoA8 Direct Atomic Scale Imaging and Spectroscopy of the Interior and Exterior of III-V Nanowires**, ***A. Mikkelsen***, Lund University, Sweden **INVITED**

Free-standing III-V nanowires and nanotubes are likely to become central components in future electronics and photonics with applications in IT, life-science and energy[1]. A very wide variety of III-V materials and dopants can be self-assembled into complex axial and radial heterostructures - precisely tailoring their structure down to the atomic scale.

We have used Scanning Tunneling Microscopy /Spectroscopy (STM/STS) and X-ray PhotoEmission and Low Energy Electron Microscopy (XPEEM/LEEM) to study nanowires and nanowire surfaces. Previously we have developed the means to directly study the interior of III-V semiconductor nanowires by STM[2], and now we have also developed direct methods for studying also the exterior nanowire surfaces to the atomic scale with STM[3].

We describe several significant results on the fundamental limits to atomic scale interface precision in AlGaAs/GaAs nanowires heterostructures, STS measurements on the interior of these wires and new insights into the influence of the growth substrate. We present atomically resolved STM images of the outside surface of InAs nanowires with InP segments along with STS measurements on the clean surfaces. The imaged surfaces of InAs nanowires are quite intriguing as the wires grow in the wurtzite crystal phase, in contrast to the zincblende bulk phase. Further we present STM images and STS measurements of InP nanowire pn-junctions. Using XPEEM and XPS we have characterized III-V nanowire surface chemistry and electronic properties and investigated the influence of various ultra-thin dielectrics to reduce surface band-bending effects.

The structure and morphology of semiconductor nanowire surfaces down to the single atom level are significant in determining both growth and function of the wires. Diffusion and nucleation on the nanowire surfaces will directly influence the final appearance of the wires, and it has been shown that transport and optical properties of semiconductor nanowires are to a considerable extent governed by their surfaces. Scanning Tunneling Microscopy is a great tool for imaging both geometric and electronic structure with high resolution, however direct atomically resolved STM studies of nanowire surfaces is very difficult. Still having overcome these problems (as in the present study) and by also applying synchrotron based spectroscopy/microscopy we obtain fascinating new insights into the interplay between nanowire growth, structure and function.

[1] C.M. Lieber and Z.L. Wang, MRS Bull. 32, (2007) 99

[2] A. Mikkelsen et al, Nature Mater. 3 (2004) 519 ; L. Ouattara et al, Nano Lett. 7 (2007) 2859

[3] E. Hilner, et al, Nano Lett., 8 (2008) 3978

5:00pm **SS1+EM-MoA10 Passivation of Ge(100) Surface Studied by Scanning Tunneling Microscopy and Spectroscopy**, ***J.S. Lee***, *S.R. Bishop, A.C. Kummel*, University of California, San Diego

Finding a good passivant for Ge surface is critical for fabricating a Ge-based MOSFET device. Recent studies have shown that GeON or GeO_2 interfacial layers can partially passivate the Ge/high-k dielectric interface and improve the electrical properties of the device. Introducing N (GeO_xN_y or Ge_3N_4) suppresses the Ge outdiffusion from the passivation layer into the high-k oxide layer at elevated temperatures, thereby reducing the post annealing density of interface states between Ge and high-k gate oxide. To minimize the density of interface states, the GeO_xN_y or Ge_3N_4 must be formed with a minimal dangling bond density, which is challenging in a thermal oxidation or nitridation process. To investigate the bonding and electronic structures of Ge-N and Ge-O surface species, in-situ scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) experiments were performed after oxidation and nitridation. Direct nitridation was carried out on Ge(100) using an electron cyclotron resonance plasma source, both at room temperature and at 500^{o}C. The nitridation at room temperature generated nitride sites, O sites (from trace water) and Ge adatoms which pin the surface Fermi level. The Ge adatoms are created because both O and N displace Ge surface atoms in order to bond at high coordination sites. These Ge adatoms can be removed by high temperature annealing. Nitridation at 500^{o}C produced a highly ordered Ge-N structure on the surface without O sites or Ge adatoms, but the Fermi level of the n-type surface was still pinned near the valence band probably due to the surface defects caused by plasma damage. Oxidation of Ge(100) was studied using a differentially pumped H_2O dosing system and the results were compared with our previous study on O_2 dosing of Ge(100). The H_2O dosed surface showed dark –OH adsorption sites with very few Ge adatoms, while the O_2 dosed surface had the equal densities of Ge adatoms and O sites. Annealing the H_2O/Ge(100) surface to 300^{o}C induces formation of bright Ge oxide sites which are slightly taller than Ge adatoms. However, both H_2O and O_2 dosing form GeO sites which are observed in STS to pin the Fermi Level. DFT calculations are being performed to determine the ordered nitride structure. In addition, the e-beam or ALD deposition of Ge_3N_4 or GeO_2 are being studied since they may form passivation layers without Ge displacement, plasma damage, and GeO, thereby unpinning the Fermi level.

5:20pm **SS1+EM-MoA11 Surface-driven Method for Incorporation of Mn into Ge Quantum Dots**, ***C.A. Nolph***, *K.R. Simov, P. Reinke*, University of Virginia

Magnetically doped nanostructures and quantum dots are important building blocks in future spintronic devices. We study the feasibility of magnetic doping of Ge quantum dots with Mn, an element with a large magnetic moment. A surface-driven route for Mn incorporation in Ge quantum dots promises superb control of the doping process. The Ge quantum dots are known to grow by strain-driven self-assembly (Stranski-Krastanov growth). Two pathways for Mn-doping have been identified: firstly, trapping of Mn at the Si-Ge interface and incorporation during quantum dot growth, and secondly, the deposition of Mn on the Ge quantum dot surface and dissolution of Mn during an annealing process. The first route requires a precise control of the Mn-bonding state at the Si(100) 2x1 substrate prior to the growth of quantum dots. Mn was deposited on Si(100) 2x1 and the surface phase diagram was determined across several temperature regimes and monitored with scanning tunneling microscopy. Mn-wire structures which formed at room temperature degrade and agglomerate to form Mn-clusters (115 - 270°C ± 30°C), then Mn moves into subsurface sites (316°C ± 38°C), and the onset of Mn-silicide formation is observed at about 342 - 416°C. This sequence is driven by the kinetics of the surface reaction between Mn and Si. A photoelectron spectroscopy study of the Si-Mn and the Si-Mn-Ge interface yields further insight into the bonding at the respective interfaces. The second route to dope quantum dots, namely the room-temperature deposition of Mn on Ge quantum dots, reveals the formation of Mn clusters, whose position is defined by the reconstruction of the Ge{105} facets. The diffusion of Mn on Ge(100) and Ge{105} facets, and into the Ge quantum dots is observed with STM during the annealing process. Our observations offer a comprehensive understanding of the Mn-interaction with all surfaces of relevance in the Si-Ge quantum dot system. The feasibility of the surface-driven route for Mn doping of Ge quantum dots will be discussed.

Surface Science
Room: N - Session SS2-MoA

Formation & Reactivity of Nanoclusters
Moderator: G.B. Fisher, University of Michigan

2:00pm **SS2-MoA1 Nanoplasmonic Sensing of Metal Hydride Formation and Catalytic Reactions on Metallic Nanoparticles**, *E.M. Larsson, C.M. Langhammer, B.H. Kasemo*, ***I.L. Zoric***, Chalmers University, Sweden

A novel, nanoplasmonics-based optical sensing platform for real time studies of nanoparticle processes is described. Examples are presented for (i) surface catalytic reaction kinetics on nanoparticles and (ii) formation of a new phase in metal hydride forming nanoparticles. The remarkably sensitive and very versatile sensing platform consists of plasmonic sensing particles (Au nanodisks, D=76nm and h=40 nm, prepared on a transparent substrate), covered by a 10nm dielectric film onto which the nanoparticles to be studied are deposited (in the present case Pd or Pt, with a size range from 2 nm-10nm). The key to the sensing is utilization of localized surface plasmon resonances (LSPR). The LSPR of the sensing nanoparticle sensitively measures changes of the surface coverage (sensitivity <0.05ML) or the formation of the new phase in the studied nanoparticles via shifts in the LSPR extinction spectra. The versatility of this method is illustrated with the following examples:

a) Hydrogen absorption/desorption (hydride formation) studies of Pd nanoparticles in the size range 2-10nm. The main result from these studies includes the size dependent thermodynamics (p-C-T diagram) and kinetics of the H/Pd nanoparticle (1-5 nm) system. The kinetics exhibit a power and power-exponential size dependence of the time scales for the hydrogen uptake and release processes. The uptake is in agreement with Monte Carlo simulations of diffusion controlled hydriding kinetics, while the release (desorption) is explained by the effect of surface tension on the activation energy for hydrogen desorption from the nanoparticle.

b) Kinetic studies of CO and H_2 oxidation on Pt nanoparticles with particular emphasis on kinetic phase transition phenomena in these reactions. The latter occur as one varies reactant concentrations but keeps the total amount of reactants constant and are recognized by a sudden transition from oxygen covered nanoparticle surfaces at low CO (H_2) concentration, to high CO or H coverage for low O_2 concentrations,

c) NO_2 storage and conversion to N_2 on Pt/BaO. In this case NO_2 storage and conversion kinetics is followed via changes in the LSPR resonance of the Au sensing particles, coated with a thin layer of BaO onto which Pt nanoparticles were deposited. Exposure of the sensor to the gas mixture of NO_2+O_2 leads to a conversion of BaO to $Ba(NO_3)_2$ (NO_x storage) leading to a change of refractive index of the material surrounding the sensing nanoparticle. This leads to a LSPR peak shift that is monitored. Exposure to H_2 converts the stored NO_2 to N_2. Reversible changes were monitored for such NO_2 oxidation/reduction cycles.

2:20pm **SS2-MoA2 On the Role of Pd Ensembles in Selective H_2O_2 Formation on PdAu Alloys**, ***H. Ham***, *G. Hwang*, University of Texas at Austin

Bimetallic Pd-Au alloys have been found to significantly increase catalytic efficiency, compared to the monometallic Pd and Au counterparts, in various reactions including direct synthesis of H_2O_2 from H_2 and O_2 and production of vinyl acetate monomers. Recent evidence suggests that the reactivity of bimetallic catalysts would be governed by creation of unique mixed-metal surface sites [the so called ensemble effect] and/or electronic structure change by metal-metal interactions [ligand effect], while mechanisms underlying the alloying effect still remain unclear. Very recently, the role played by Pd monomers in the direct H_2O_2 synthesis has also been studied using density functional theory calculations, yet detailed reaction mechanisms associated with Pd atomic arrangements are still lacking. In this talk, we will present some recent theoretical results we have on the role of Pd ensembles in determining the selectivity of direct H_2O_2 synthesis. Using periodic density functional theory calculations, we find that the H_2O_2 formation selectivity can be governed by the spatial arrangements of Pd and Au surface atoms, particularly the availability of Pd monomers surrounded by less active Au atoms. Our calculations suggest that the large activity difference between Pd and Au atoms is a key factor for selective H_2O_2 formation, by suppressing O-O bond scission. This work hints the importance of knowing how to properly tailor Au reactivity for achieving wanted reactions, while the relative activities of Au and Pd surface atoms can be a function of subsurface layer composition as well as catalyst size and shape.

2:40pm **SS2-MoA3 Well-defined, Highly Uniform Metallic Nano-Structures as Selective Heterogeneous Catalysts and Platforms for Chemical Characterization**, *S. Linic*, ***Christopher***, University of Michigan **INVITED**

I will present our recent work where we explored potential utilization of highly uniform metallic nano-structured materials as selective heterogeneous catalysts. The advantage of these materials compared to conventional catalytic materials is that their structure can be controlled with almost atomic precision, and that it is possible to synthesize highly homogeneous structures. We demonstrated some of these advantages recently when we showed that well-defined, tailored Ag nano-structures are much more selective in heterogeneous epoxidation of ethylene to form ethylene oxide (EO) (ethylene + ½ O_2 → EO) than conventional industrial catalysts.

We showed using quantum chemical Density Functional Theory (DFT) calculations, where we studied critical elementary chemical steps that govern the selectivity to EO in the process, that the Ag(100) surface should be inherently more selective than the Ag(111) surface. We note that catalytic particles, synthesized using conventional synthesis procedure and currently used in commercial ethylene epoxidation process, are dominated by the (111) surface. To synthesize Ag nano-structures which are dominated with the Ag(100) faces, we employed a synthesis procedure which uses organic stabilizer molecules to direct the growth of the nano-structure in a particular direction and to control the surface facets that terminate the nano-structure. This synthetics strategy allowed us to synthesize well-defined and highly uniform Ag nano-wires and nano-cubes which are dominated by the (100) facet. Subsequent experiments showed that Ag nano-wires and nano-cube catalysts can achieve selectivity to EO, which is, at differential conversion, by ~ 40 % higher than for conventional Ag catalysts.

We have also recently started exploring these metallic nano-structures as possible platforms for chemical characterization. The features of these nano-structures that are particularly appealing are: (i) the nanostructures are well defined on atomic level, and their surface to volume ratio is fairly high, which makes these structures inherently better suited for the studies of surface chemical processes compared to traditional single crystal model systems, which are while very well defined, characterized by low surface to volume ratio, (ii) we can synthesize the nanostructures with high degree of uniformity in size and shape, which rules out possible effects due to diversity in size and shape, i.e. these, (iii) the nanostructures are effective scatterers of electromagnetic radiation which make them suitable as platforms for a number of chemical characterization techniques including surface enhanced Raman (SERS) or IR spectroscopies. We will demonstrate the utility of the nano-structures for chemical characterization by a way of an example, where we monitored in-situ ethylene epoxidation.

3:40pm **SS2-MoA6 2009 AVS Peter Mark Memorial Award Lecture - Towards the Understanding of Catalytic and Vibrational Properties of Metal Nanostructures**, ***B.R. Cuenya****, University of Central Florida **INVITED**

Metallic nanostructures are of great interest in many scientific fields due to their novel size-dependent physical and chemical properties. The origin of the enhanced catalytic reactivity and selectivity displayed by small metal nanoparticles is yet to be explained. However, it is generally agreed that the design of the next generation of nanocatalysts requires detailed knowledge of the correlation between their reactivity and their physical properties such as morphology, electronic structure, chemical composition, and interactions with their support. Intriguing effects including phonon confinement and phonon localization at interfaces have also been observed in low dimensional systems . Such modifications of the vibrational density of states of nanoscale materials are of scientific and technological relevance, because they profoundly affect their thermodynamic properties. In addition, their understanding could help further our insight in the field of catalysis, since phonons might play a decisive role in certain chemical processes. To systematically study these effects, homogeneous and size-selected nanostructures are needed. Diblock-copolymers can aid the synthesis of such well-defined nanoscale systems.

The first part of my talk will illustrate the formation, stability, as well as the electronic and catalytic properties of size- and shape-selected Au, AuFe, Pt, and Pt-M (M = Au, Fe, Ru and Pd) nanoparticles synthesized by micelle encapsulation. CO oxidation and alcohol decomposition and oxidation have been used as model reactions. Emphasis will be given to the role of the nanoparticle support and the oxidation state of the active catalytic species in their reactivity.

In addition to changes in reactivity, nanostructuring materials also affects their vibrational properties. The second part of my talk will discuss the size- and composition-dependent vibrational dynamics of ^{57}Fe, ^{57}FePt, and ^{57}FeAu clusters as well as of nanostructured metal multilayers prepared by molecular beam epitaxy in UHV. The phonon density of states of those systems will be extracted from nuclear resonant inelastic X-ray scattering measurements. An enhancement of the density of low- and high-energy phonon modes as well as non-Debye-like behavior was observed on ^{57}Fe clusters. The latter effects were found to depend on the chemical nature of the surface shell on the nanoclusters. Thickness-dependent phonon confinement and interface localization effects were detected on nanoscale ^{57}Fe/M multilayers (M = Cu, Pd or Ag). All these effects show the unique physical properties of metal nanoparticles, and their promise in technological applications.

Website: http://www.physics.ucf.edu/~roldan

4:20pm **SS2-MoA8 Growth, Composition and Surface Chemistry of Ni-Au Clusters on TiO_2(110)**, ***D.A. Chen***, *S.A. Tenney, J.S. Ratliff, C.C. Roberts*, University of South Carolina

Scanning tunneling microscopy (STM) studies show that bimetallic Ni-Au clusters supported on TiO_2(110) are formed by deposition Au on top of Ni clusters. Due to the higher mobility of Au compared to Ni atoms on TiO_2(110), deposited Au is nucleated at existing Ni clusters. Low energy ion scattering experiments demonstrate that the surface of the bimetallic clusters is predominantly Au for compositions above 50% Au, but 10-15% Ni also exists at the surface. The presence of Ni at the surface is in contrast to the expected Ni core-Au shell structure based on bulk thermodynamics; the large bulk miscibility gap for the two metals and the lower surface free energy of Au compared to Ni predicts that only Au should be at the cluster surface. Furthermore, adsorption of CO onto the Ni-Au clusters appears to induce the diffusion of Ni to the cluster surface. After annealing the Ni-Au clusters to 800 K and above, the clusters become encapsulated by stoichiometric titania. Although Ni and Au clusters annealed to 1000 K are roughly the same size, the addition of Ni to the Au clusters suppresses cluster sintering.

4:40pm **SS2-MoA9 Deposition of RuSn Nanoparticles onto a Al_2O_3/Ni_3Al(111) Surface from a Gas Phase Organometallic Precursor**, ***A. Uhl***, University of Illinois at Chicago, *E. Trufan, R.D. Adams*, University of South Carolina, *R.J. Meyer, M. Trenary*, University of Illinois at Chicago

Scanning tunneling microscopy (STM) was used to characterize RuSn nanoparticles deposited from a gas phase organometallic precursor $(Ru_3(CO)_9(\mu\text{-}SnPh_2)_3)$ onto an Al_2O_3 film grown on a Ni_3Al(111) substrate. This novel method allows for the specific preparation of small metal clusters that range between single atoms and larger, bulk-like particles. It also assists in bridging the gap between previous studies based on metal evaporation and industrial catalysis, where the use of precursor compounds for the active species is common. The STM images of the Al_2O_3/Ni_3Al(111)

---

* Peter Mark Memorial Award Winner

substrate prior to the exposure of the precursor show two distinct areas, with the first one exhibiting the dot structure of the alumina film, as reported in the literature. The second area does not exhibit any regular structure. After exposing the sample to the precursor at room temperature, the precursor was found to adsorb preferentially onto the second area, but also on the first area in significant amounts. In a subsequent series of images acquired for increasingly higher annealing temperatures, the discrepancy between the two areas in the interaction with the adsorbates is strongly increased. While the surface with the dot structure becomes almost fully depleted of the adsorbates, except for a few small (up to 3 nm in diameter) and roundish protrucions, the other area is covered by larger polygonal protrusions. Similarly shaped depressions in the surface are observed along with the protrusions. A control experiment in which the bare Ni$_3$Al(111) surface was exposed to the precursor indicates that the second area of the Al$_2$O$_3$/Ni$_3$Al(111) surface consists of patches of bare metal. A striking difference between the protrusions on the oxide and the metal is that the size of the latter increases dramatically with increasing annealing temperature, while the former do not grow at all. Nevertheless, both features are observed even up to 925 K, from which it is concluded that the annealing removes the ligands from the metal centers of the precursor molecules, after which the metal nanoparticles can form. These results show that by using an organometallic precursor, small uniform metal nanoparticles with high thermal stability can be successfully deposited onto an oxide thin film. This paves the way for subsequent studies of the surface chemistry associated with model oxide-supported metal catalysts consisting of metal nanoparticles of a uniform size.

5:00pm **SS2-MoA10 Formation, Thermal Stability and In-situ Gas Phase Catalytic Properties of Supported Au, Fe, and Au$_x$Fe$_{1-x}$ Nanoparticles**, ***L.K. Ono***, *A. Naitabdi*, *B. Roldan Cuenya*, University of Central Florida

Metal-loaded diblock-copolymer micelles have been used to synthesize size-selected self-assembled Au, Fe, and Au-Fe nanoparticles (NPs). In-situ scanning tunneling microscopy (STM) and X-ray photoelectron spectroscopy (XPS) measurements were performed to investigate the formation and thermal stability of Au$_x$Fe$_{1-x}$ (x = 1, 0.8, 0.5, 0.2, 0) NPs supported on TiO$_2$(110) [1]. Upon step-wise annealing from 300°C to 1060°C, a remarkable thermal stability of the Au-Fe NPs was observed, maintaining their original hexagonal spatial arrangement on the TiO$_2$ surface up to 900°C. A majority phase of a gold-iron alloy (solid solution) was achieved for our Au$_{0.5}$Fe$_{0.5}$ NPs in the temperature range of 700°C - 800°C, and for Au$_{0.2}$Fe$_{0.8}$ NPs at 800°C, while a phase mixture of bcc Fe and Au-Fe alloy was observed for the Au$_{0.8}$Fe$_{0.2}$ system at 800°C - 900°C. For all samples the segregation of Au atoms towards the NP surface was detected upon high temperature annealing (800°C) in vacuum. Nearly complete Au desorption was observed by XPS at 900°C for Au$_{0.2}$Fe$_{0.8}$ NPs, at 1000°C for Au$_{0.5}$Fe$_{0.5}$ NPs, and at 1060°C for Au$_{0.8}$Fe$_{0.2}$ NPs. The enhanced thermal stability of Au in the Au$_{0.8}$Fe$_{0.2}$ NPs is believed to be related to the formation of core(Fe)/shell(Au) structures. Furthermore, contrary to the case of pure Fe or Fe-rich NPs where nearly complete Fe desorption or Fe diffusion into TiO$_2$ was observed at 1000°C, an Fe signal was detected at this temperature for the Au-rich samples (Au$_{0.8}$Fe$_{0.2}$ and Au$_{0.5}$Fe$_{0.5}$).

The reactivity of our pure Au, pure Fe, bimetallic Au-Fe and a sample with a mixture of pure Au and pure Fe NPs will be compared via in-situ (UHV) temperature programmed desorption measurements. CO oxidation has been used as probe reaction.

[1] A. Naitabdi, L.K. Ono, F. Behafarid, B. Roldan Cuenya, J. Phys. Chem. C 113 (2009) 1433.

5:20pm **SS2-MoA11 Secretive Lives of Multi-component Nanoparticles during Reactions**, ***F. Tao****, *M. Grass*, *D. Butcher*, *J.R. Renzas*, *Y. Zhang*, *C. Tsung*, *S. Aloni*, *M. Salmeron*, *G.A. Somorjai*, Lawrence Berkeley National Lab

The bimetallic catalyst is one important category of heterogeneous catalysts for numerous industrial processes and energy conversion. Surface structure and chemistry of three bimetallic catalysts, Rh-Pd, Rh-Pt, and Pd-Pt nanoparticles during catalysis, oxidation, and reducing reactions have been systematically studied in-situ using XPS in a Torr pressure range and high resolution TEM. The Rh$_x$Pd$_{1-x}$ and Rh$_x$Pt$_{1-x}$ nanoparticles undergo reversible changes in both atomic fractions and chemical states corresponding to the switch of reaction environments between oxidizing and reducing conditions. Rh atoms in Rh$_x$Pd$_{1-x}$ and Rh$_x$Pt$_{1-x}$ segregate to surface layers and are largely oxidized in oxidizing conditions while in reducing atmospheres the Pd atoms in Rh$_x$Pd$_{1-x}$ and Pt atoms in Rh$_x$Pt$_{1-x}$ diffuse to the surface regions and Rh atoms are largely reduced. In contrast to Rh$_x$Pd$_{1-x}$ and Rh$_x$Pt$_{1-x}$, no significant segregation of Pd or Pt atoms was found in Pt$_x$Pd$_{1-x}$ nanoparticles; Pd atoms are alternatively oxidized and reduced under oxidizing and reducing conditions, whereas Pt atoms do not. The capability of restructuring nanoparticles through chemical reactions illustrates the flexibility of the structure of bimetallic nanoparticle catalysts and suggests a new method for the development of new catalysts.

Reference: F. Tao et al. 322, 932 (2008)

Thin Film
Room: A8 - Session TF1+PV-MoA

Chalcogenide Photovoltaics
Moderator: A. Rockett, University of Illinois, Urbana-Champaign

2:00pm **TF1+PV-MoA1 Growth and Structure of RF Sputter-Deposited Cadmium Sulfide (CdS) Thin Films**, ***R.S. Vemuri***, *D. Zubia*, *C. McClure*, *C.V. Ramana*, University of Texas at El Paso

Cadmium sulfide (CdS) is a group II–VI semiconductor, which finds many scientific and technological applications. CdS thin films are particualrly interesting for application in large area photovotaics in addition to field-effect transistors, visible spectral range photoconductors, optical filters and nonlinear integrated optical devices. However, growth and optimization of conditions to produce high-quality CdS layers is important for enhanced photovoltaic device performances. In the present work, ordered cubic structured CdS films for application in CdTe/CdS solar cells were produced using RF magnetron sputtering. Pure CdS target was employed for sputtering. Two sets of CdS films were deposited: (1) at varying powers, in the range of 70-130 W, at constant Ar pressure of 7 mTorr, and (2) at varying Ar pressures, in the range of 5-20 mTorr at a constant power of 100 W. A detailed structural characterization was made to understand the effect of processing conditions on the morphology evolution, grain size, and crystal structure of the CdS films. High-resolution scanning electron microscopy (HRSEM) measurements revealed the smooth surface morphology of the CdS layers both as a function of sputtering power and Ar-pressure. CdS films grown at 70-130 W were found to be nanocrystalline, exhibiting grain-size (L) dependence on the sputtering-power (W). L increased with W yielding the highest average L=145 nm at 105 W. Further increase in W resulted in decreasing L. Similarly, under varying Ar pressure, the highest L (~138 nm) values were found at 5 mTorr. X-ray diffraction (XRD) analysis indicated that the entire set of deposited CdS films exhibit highly oriented cubic structure. L values evaluated from XRD are in good agreement with the HRSEM results. The optical characteristics were evaluated and a functional relationship between growth conditions and band gap, useful to tailor the CdS films for desired solar-cell application, was found. The results obtained will be presented and discussed.

2:20pm **TF1+PV-MoA2 Characterization of Photovoltaic Thin Films Materials Using RF GD-OES and LA ICP-MS**, ***F. Li***, *S. Anderson*, Air Liquide - Balazs, *P. Hunault*, HORIBA Jobin Yvon

Photovoltaic thin film materials have been characterized by a number of traditional vacuum techniques; Auger, XPS, SIMS, and GD-MS to name only a few. Depth profiles of solar cell modules, contamination in the sputtering targets or surface stoichiometry of photovoltaic thin films are specific application examples which predicate the technique best suited for the data requirement. The evolution of thin films with new chemistries and the importance of surface modification for photovoltaic applications provide a continuing need for thin film analyses along with an avenue for new analytical tools.

In this paper we will discuss the application of two non-traditional surface and material analysis techniques for the photovoltaic solar industry, glow discharge optical emission spectroscopy (RF GD-OES) and laser ablation inductively coupled plasma mass spectrometry (LA ICP-MS). The RF GD-OES and LA ICP-MS techniques enable direct analysis and depth profiling of a variety of conductive and nonconductive materials and photovoltaic thin films such as SoGSi, CdTe, CIGS, and TCO. With each technique, the ability to simultaneously depth profile more than 40 elements is possible. RF GD-OES and LA ICP-MS are much faster and more cost effective for depth profiling than SIMS. When using the techniques as an elemental survey technique, each analysis is more sensitive and also much faster than Auger and XPS.

Additional specific advantages of RF GD-OES and LA ICP-MS will also be discussed. Using radio frequency (RF) plasma for analytical signal generation, these techniques do not have the surface equilibrium issues seen with other surface analytical techniques such as SIMS. The charging effect that can cause issues with electron and ion beam techniques is also avoided.

---

* TFD Young Researcher Award Winner

Additionally, there are no artifacts in their sputtering processes, especially on the top surface. Therefore, the surface stoichiometry of some solar thin films before and after chemical treatment can be reliably characterized. This feature is extremely important for surface modification projects in an effort to produce far more efficient photovoltaic thin films. Finally both RF GD-OES and LA ICP-MS don't require any sample preparation unlike GD-MS, thin films and materials can be directly characterized in their natural states against NIST traceable standards.

2:40pm **TF1+PV-MoA3 Multi-technique Lateral and Vertical Surface Characterisation of Thin-film Photovoltaics**, ***A.J. Roberts***, Kratos Analytical Ltd, UK, *C.J. Moffitt*, Kratos Analytical Inc., *J.W. Pankow*, National Renewable Energy Laboratory

Thin-film photovoltaic production is an important and fast growing field in energy technology. The most widely applied thin-film photovoltaic technology is based on the use of cadmium telluride / cadmium sulfide (CdTe/CdS) heterojunctions and although research in CdTe dates back to the 1950s the challenges associated with junction quality and electrical contacting have not been well addressed. Both vertical (depth) and lateral composition of thin film PV devices is of great importance for optimum performance.

The cadmium tin oxide (CTO)/zinc tin oxide (ZTO) bilayer structure is an alternative to traditional tin oxide front contacts and provides lower resistance and better light transmission. Modern multilayer stacks such as CdTe/CdS/ZTO/CTO/glass have lead to the best reported cell efficiencies of ~16.5% but disparate differences in efficiencies can be observed for devices made from films located within even a cm of each other and back contacted in identical fashion. This work presents the use of photoemission spectroscopies combined with Ar+ ion depth profiling to characterise a CdTe/CdS/ZTO/CTO/glass multilayer sample. X-ray photoelectron spectroscopy (XPS) depth profiling has been used to generate elemental and chemical information as a function of depth through the layer and interface regions using sputtering conditions chosen minimize surface roughening and knock on phenomena that can cause difficulties in discerning between true depth variations and sputter induced artifacts when analyses are done under traditional sputter conditions. In combination with XPS, ultraviolet photoemission spectroscopy (UPS) depth profiling has been used to measure the pseudo work-function of the layers and interface regions, allowing a pseudo work-function depth profile to be generated.

As well as vertical compositional charaterisation the lateral composition has been investigated for a different thin-film PV system comprising Cu:In:Ga:Se (CIGS)/Mo/glass. Changes across the surface are undesirable in the manufacturing process as small differences in Cu/(In+Ga) or Ga/(In+Ga) can compromise ultimate device efficiency. These compositional changes typically occur over centimeter scales necessitating mapping over >5x5 cm. The multi-technique approach to surface characterisation of these thin film photovoltaics has provided chemical, elemental, pseudo work-function as a function of depth and lateral compositional information from two different thin film photovoltaic systems.

3:00pm **TF1+PV-MoA4 XPS Band Offset Measurements of ZnO, CdTe, and CuSCN for Application in Nanostructured Photovoltaics**, ***T.C. Kaspar***, *T. Droubay, J.E. Jaffe, V. Shutthanandan, W. Jiang, S.A. Chambers, G.J. Exarhos*, Pacific Northwest National Laboratory

All photovoltaic devices require efficient electron-hole separation, transport, and collection. It is relatively straightforward to experimentally determine the charge transport properties of the individual component materials in a given cell design, allowing optimization. However, the charge transport across heterojunction interfaces between component materials is just as critical for overall cell performance. The electron or hole injection efficiency is determined by the band structure alignment at the interface; optimization of the interface for facile charge injection requires detailed knowledge of the band offsets, which cannot easily be determined by electrical transport measurements. We utilize high resolution x-ray photoelectron spectroscopy (XPS) to directly quantify the band offsets of heterojunctions relevant to photovoltaic cells. Nanostructured extremely thin absorber (ETA) photovoltaic devices have been proposed as an inexpensive alternative to current single-crystal device technology, although the devices reported thus far suffer from low conversion efficiency. Thus, materials relevant to ETA devices were chosen for study: n-ZnO as the electron transporter, solid-state p-CuSCN as the hole conductor, and CdTe as the photon absorber. High quality ZnO thin films were deposited by pulsed laser deposition (PLD) on F:SnO_2/glass substrates for XPS band offset measurements. The band offsets were determined as a function of ZnO conductivity, and strategies for improved electron conduction across the interface will be discussed. In addition, the materials properties of CuSCN were thoroughly characterized, and its electronic structure was compared to density functional theory (DFT) calculations. The calculations show an indirect bandgap of 2.7eV and highly anisotropic charge transport with the unusual prediction that hole mobility exceeds the electron mobility. Avenues to improve hole conduction through the introduction of defects in CuSCN were explored.

3:40pm **TF1+PV-MoA6 Effects of Cu Doping Level in ZnTe:Cu Back Contacts on Cu Diffusion and CdTe Solar Cell Performance**, ***J.N. Duenow***, *R.G. Dhere, S.E. Asher, W.K. Metzger, J. Li, T. Moriarty, T.A. Gessert*, National Renewable Energy Laboratory

CdTe photovoltaic (PV) cells require a low-resistance back contact for optimal device performance. Cu-doped ZnTe (ZnTe:Cu) has been implemented successfully as an ohmic back-contact interface layer to CdTe, enabling PV cells with efficiencies of 14%. ZnTe:Cu offers the additional advantage of being easily manufactured by vacuum processing, which enables highly controlled, reproducible films. Although CdTe devices have been made without Cu-containing contacts, devices with Cu contacts have generally exhibited higher performance. Controlled Cu diffusion from the back contact is known to be critical for optimal performance. Sufficient Cu is required for doping the CdTe absorber to provide a strong electric field in the junction region. Excessive Cu, however, can lead to poorer collection by narrowing the depletion region to the extent that few minority carriers are generated within a diffusion length of the depletion region. Cu may also adversely affect the junction by diffusing into the CdS window layer.

Previous studies of Cu diffusion from ZnTe:Cu back contacts have been performed at NREL using a fixed doping level of Cu in ZnTe, but altering Cu diffusion by changing the deposition temperature or film thickness. In this study, we instead deposit ZnTe:Cu films from targets containing a range of Cu amounts—from 0.45 to 5 wt.%—while holding the temperature and film thickness constant. Capacitance-voltage, red-light-biased quantum efficiency, and secondary-ion mass spectrometry depth-profile measurements will indicate the net acceptor concentration in the CdTe and the degree of Cu diffusion as a function of the Cu density in the back-contact interface layer. Minority-carrier lifetime measurements will be used to correlate the effects of Cu density to the carrier recombination rate.

4:00pm **TF1+PV-MoA7 Surface and Interface Properties ZnTe-based Solar Cell**, ***F. Fang***, *B.E. McCandless, R.L. Opila*, University of Delaware

In order to substantially reduce the capital costs of present crystalline silicon photovoltaics, alternative thin film solar cell (TFSC) devices are favored because of the inexpensive materials, simple material preparation, and low-cost large area fabrication. There is interest in growing polycrystalline thin films of II-VI direct band gap semiconductors, such as CdS/CdTe. TFSCs are well studied and currently being used for manufacture of commercial scale solar modules. Here, we are proposing a heterojunction system *n*-ZnSe/*p*-ZnTe as a wide band gap TFSC ($E_G > 2$ eV) for potential application in tandem cells. This provides an efficiency enhancement for future generation photovoltaics, provided the wide band gap cell efficiency can be increased. In addition, we are using Close Space Sublimation (CSS), which is a low-cost deposition method already demonstrated for high efficiency and commercial CdTe TFSC.

Our ZnSe/ZnTe TFSC is a heterojunction device with a high density of defect states at interfaces which can provide interface recombination centers; also the grain boundaries in polycrystalline semiconductor films act as shallow and deep defect levels within the bandgap and create different recombination mechanisms than radiative band-to-band recombination in ideal crystalline devices. As a result, minority carrier collection relies on the built-in electric field, and results in voltage-dependent collection of photo-generated current. Therefore, it is crucial to form a high quality diffused junction. Some earlier work reported a diffusion voltage of 1.70 eV for single crystal ZnSe/ZnTe structure, which suggests that open circuit voltage, $V_{OC} > 1$V is feasible. We have used Al-Kα X-ray photoelectron spectroscopy and Soft (Ultra-violet) X-ray photoelectron spectroscopy (Synchrotron Light Source) to investigate the surface chemistry and valence band structures of the as-deposited films, scanning electron microscopy (SEM) to investigate the surface and cross-section morphology, energy-dispersive X-ray spectroscopy (EDX) to verify the chemistry. Surface oxides on ZnSe have been identified and their effects on interface band offset are evaluated. A significant valence band maximum shift is also observed with UPS which indicates an increased maximum open circuit voltage of the junction. This result is consistent with our I-V testing. Better devices with $V_{OC} > 600$ mV and photocurrent $J_{SC} > 5$ mA/cm^2 were only obtained for films with ZnTe deposited immediately after ZnSe, i.e., no time for oxide formation. More detailed understanding of the chemistry and interfacial band structure are being investigated and used to guide a path to improved conversion efficiency.

4:20pm **TF1+PV-MoA8 Issues of Large-Scale Photovoltaic Energy Production from Thin-Film CdTe Devices**, ***T.A. Gessert***, National Renewable Energy Laboratory **INVITED**

It is now widely accepted that thin-film photovoltaic (PV) devices will be important contributors of new US electricity generation. The annual production of PV devices needed to meet conservative U.S. Department of Energy goals for 2050 represents ~100 square miles of active module area (20 GW), or ~200 times the total area of photovoltaic modules installed in the US by 2004. However, if the rate of growth observed in PV module production for the past eight years continues, 100 square miles of annual US PV production could be achieved as early as 2018. Further, the amount PV installed by 2036 could generate the entire 2004 US Total Energy Consumption (~100 Quadrillion BTU's, i.e., the combined energy consumed in the US from petroleum, coal, natural gas, nuclear, and all renewable sources). Regardless of what assumptions are made, PV represents a significant future market, especially for thin-film modules based on CdTe and related process technologies. This talk will discuss CdTe thin-film PV devices within the context of the major PV technologies in production today, and indicate areas where improved material and device understanding would be beneficial.

5:00pm **TF1+PV-MoA10 Novel Solar Cells based on a $ZnGeAs_2$ Absorber Layer**, ***T.J. Peshek***, National Renewable Energy Laboratory and Arizona State University, *T.J. Coutts, T.A. Gessert,* National Renewable Energy Laboratory, *Z.Z. Tang, L. Zhang, N. Newman, M. van Schilfgaarde*, Arizona State University

We present the latest results on the development of a novel thin film solar cell based upon the direct gap chalcopyrite semiconductor $ZnGeAs_2$. This material has long been viewed as a promising solar material for high efficiency multijunction cells due to it being lattice matched to GaAs and having a band gap of about 1.1 eV. In light of recent advances in single junction solar cells based on chalcopyrite materials such as $CuInSe_2$ we have fabricated the first, to our knowledge, single junction cell based on $ZnGeAs_2$. Initial tests show the devices to have low conversion efficiencies because the photogenerated currents are low. However, we find that the open-circuit voltage in our first tests is approximately 0.135 V. It is our hypothesis based on the J-V curves that the current sourced by the cell can be improved significantly at this point by reducing the series resistance of the device and minimizing any shunts that seem to be present in these devices. The cell is structured according to the superstrate configuration using RF sputtered CdS as the n-type buffer layer. The p-type $ZnGeAs_2$ absorber was deposited at about 600 K by pulsed laser deposition.

This work is supported by DOE-EERE grant DE-FG36-08GO18002, NREL, and Arizona State University. This abstract subject to governmental rights.

Thin Film
Room: B3 - Session TF2-MoA

Thin Films: Growth and Characterization II
Moderator: S.B. Sinnott, University of Florida

2:00pm **TF2-MoA1 Creation of All-Diamond Core-Shell Particles by Layer-by-Layer Deposition for use in Solid Phase Extraction and Chromatography**, ***G. Saini***, *L.A. Wiest, R.C. Davis,* Brigham Young University, *A. Dadson, M.A. Vail,* U.S. Synthetic, *M.L. Lee, M.R. Linford*, Brigham Young University

We report the formation of all-diamond, core-shell particles for solid phase extraction (SPE) made via layer-by-layer deposition. The process begins with the amine functionalization of microdiamond by its immersion in an aqueous solution of an amine-containing polymer. The amine functionalized microdiamond is then immersed in an aqueous suspension of the nanodiamond, which leads to adsorption of nanodiamond. Alternating immersion in the solution of amine containing polymer and in the suspension of nanodiamond is continued until the desired number of nanodiamond layers is formed around the microdiamond. Finally, the core-shell particles are crosslinked with 1,2,5,6-diepoxycyclooctane to increase their mechanical and chemical stability. Core-shell particles are characterized by diffuse reflectance infrared Fourier transform spectroscopy (DRIFT), environmental scanning electron microscopy (ESEM), X-ray photoelectron spectroscopy (XPS) and Brunauer Emmett Teller (BET) surface area and pore size measurements. Core-shell diamond particles have much higher surface area and analyte loading capacity as measured in SPE than non-porous solid diamond particles. For example, for 50-70 µm core-shell particles containing 9 bilayers of poly(allylamine) (PAAm) and 100-250 nm nanodiamond, which can be made relatively easily, a ca. 21-fold increase in BET surface area and 80-fold increase in analyte loading capacity by SPE was observed in comparison to non-porous solid diamond particles.

2:20pm **TF2-MoA2 Plasma Polymer Film Behavior in Ethanol: A Multi-Technique Investigation**, ***L. Denis***, *D. Thiry,* University of Mons, Belgium, *D. Cossement,* Materia Nova Research Center, Belgium, *P. Gerbaux,* University of Mons, Belgium, *F. Brusciotti, I. Van De Keere, V. Goossens, H. Terryn,* Vrije Universiteit Brussel, Belgium, *M. Hecq, R. Snyders*, University of Mons, Belgium

Primary amine-based plasma polymer films (PPF) attract increasing interest in biotechnology since they have recently been reported to support cell growth and biomacromolecule (DNA, polysaccharides) immobilization. Since many years, the PPF chemistry has extensively been studied. Nevertheless, the behavior of these materials in solvents is not yet fully understood. For example, some works have reported the decrease of allylamine PPF thickness (Δd) after immersion in ethanol. Such a kind of observation is frequently attributed to the loss of material in the solvent. Up to now, however, such assumption remains unproved and therefore this phenomenon needs further investigations.

In this work, allylamine PPF have been synthesized at low pressure (2.67 Pa) using pulsed radiofrequency discharges varying the mean power injected in the plasma (P_{mean}). The PPF behavior in ethanol has been studied through analysis of both PPF and the resulting ethanol solution characteristics.

Δd which is inversely proportional to P_{mean} has been measured by ellipsometry. This behavior has been attributed to the increase of the PPF cross-linking density (d_{XL}) with P_{mean}. In order to evaluate d_{XL}, we have used Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and further treatment of the data by Principal Component Analysis (PCA). The results suggest an increase of d_{XL} with P_{mean}, hence supporting our assumption. Moreover, it should be noted that the PPF chemistry, evaluated by X-ray Photoelectron Spectroscopy (XPS), does not change significantly after ethanol immersion.

On the other hand, the ethanol solution has been analyzed by Gas Chromatography – Mass Spectrometry (GC-MS), a highly sensitive method (10^{-9} g/ml). The results show that there are no chemical species released by the PPF during immersion.

Therefore, our set of data suggests that Δd, observed after PPF immersion in ethanol, is mostly related to reorganization of the PPF structure and not to material dissolution in the solvent.

2:40pm **TF2-MoA3 Controlled Growth of MOFs Thin Films on Functionalized Organic Surfaces**, ***O. Shekhah***, *H. Wang, Ch. Woell, R. Fischer*, Ruhr Uni. Bochum, Germany

The fabrication of thin film coatings of metal–organic frameworks (MOFs) on surfaces is of great importance for various applications, like smart membranes, catalytic coatings, chemical sensors, and many other related nano-technological devices. The main challenge for the fabrication of such thin films is to accurately control their growth.

We will report on the development of a novel step-by-step approach for the synthesis of metal-organic frameworks (MOFs) and their deposition on functionalized organic surfaces. The approach is based on the sequential immersion of functionalized organic surfaces, alternately in solutions of the building blocks of the MOF, i.e. the organic ligand and the metal precursor. 1-3

The synthesis and growth of different types of MOFs on substrates with different functionalization like COOH, OH and pyridine terminated were studied and characterized with different techniques like IRRAS, SPR, and AFM. The IRRAS, SPR and AFM data showed a linear increase in the thickness of grown layers for each immersion cycle. The AFM and SEM data recorded for laterally patterned substrates also demonstrated that the growth of the MOF-layers is highly selective.

The dependence of MOF-deposition on the termination of the substrate was demonstrated in the case of [Cu3BTC2(H2O)n] MOF on both COOH and OH terminated surfaces, where the XRD out-of-plane (Figure 1) and the in-plane data showed the presence of a highly ordered and a preferentially oriented crystalline material, that exhibits the same structure as observed for the bulk compound.[1] This was also demonstrated for the case of the (Zn2(bdc)2(dabco)) MOF on the pyridine terminated surface.[2]

References

(1) O. Shekhah, H. Wang, S. Kowarik, F. Schreiber, M. Paulus, M. Tolan, C. Sternemann, F. Evers, D. Zacher,

R. A. Fischer and C. Wöll, J. Am. Chem. Soc., 2007, 129, 15118.

(2) D. Zacher, O. Shekhah, Ch. Wöll, R. A. Fischer, Chem. Soc. Rev., 2009, 38, 1418–1429.

(3) O. Shekhah, H. Wang, M. Paradinas, C. Ocal, B. Schüpbach, A. Terfort, D. Zacher, R. A. Fischer, Ch. Wöll, Nature Materials, in printl. 2009. DOI:10.1038/nmat2445

3:00pm **TF2-MoA4 Counterion Dependent Swelling of Redox-Active Polyelectrolyte Multilayers**, ***R. Zahn***, ETH Zurich, Switzerland, *F. Boulmedias,* Institut Charles Sadron, France, *J. Voros,* ETH Zurich, Switzerland, *P. Schaaf,* Institut Charles Sadron, France, *T. Zambelli*, ETH Zurich, Switzerland

Polyelectrolyte Multilayers (PEMs), formed by alternating layer-by-layer (LBL) deposition of polyanions and polycations, have been widely studied during the last decade. The properties of these layers can be tuned by varying the PEM composition, and thus present a promising tool for a wide range of applications.

Here we present a PEM consisting of alternating layers of Poly-L-Glutamic Acid (PGA) and Poly-(Allylamine Hydrochloride) (PAH) containing Ferrocyanide (FC) ions as electrochemically active species. The PEM buildup was monitored *in situ* using Quartz Crystal Microbalance with Dissipation monitoring (QCM-D). Ferrocyanide (FC) ions were added to the film and cyclic voltammetry was performed to oxidize and reduce the ions.

We found that oxidation and reduction of the incorporated FC ions caused the expansion and contraction of the PEM films. Applying 0.6 V caused the FC ions to be oxidized from $[Fe(CN)_6]^{4-}$ to $[Fe(CN)_6]^{3-}$, leading to a thicker and less rigid film. This was observed using electrochemical QCM-D (EC-QCM-D). Subsequent reduction of the ions caused the film to contract back to its original state. Measurements involving different counter ions showed a strong dependency on the anion species, charge, and molarity. No such effects could be shown for different cations. The swelling behavior of the PEM films is also influenced by changes in the pH of the buffer.

The observed swelling behavior is attributed to charge compensation by counter ions. Upon oxidation of the FC, anions diffuse into the PEM and replace the missing negative charge. These ions, and their accompanying hydration shell, cause an increase in the osmotic pressure within the layer, which leads to the observed swelling behavior. Depending on their thermodynamic properties (charge, hydration shell thickness, and hydration entropy), a certain fraction of the counter anions can condensate on the PAH-FC complexes and decrease the swelling. This dependency of the swelling effect on the specific interaction of the polymer to the counter ion is also verified by Attenuated Total internal Reflectance Fourier Transformed InfraRed (ATR-FTIR) spectroscopy. High ionic strengths and pH values result in partial Donnan breakdown, which allows water to enter and cations to leave the PEMs.

To conclude, we have investigated a system of electroactive PEMs. Their swelling response can be tuned by choosing different counter ions and pH conditions.

3:40pm **TF2-MoA6 Gas and Liquid Media Approaches to Low Temperature Fabrication of Aluminum Oxide Thin Films**, ***X.F. Duan***, The University of Melbourne, Australia, *N.H. Tran,* University of Western Sydney, Australia, *N.K. Roberts,* The University of New South Wales, Australia, *R.N. Lamb*, The University of Melbourne, Australia

Al_2O_3 thin films are useful in a variety of applications from gate insulators to implant prosthetic devices. They can be made in a number of different ways but usually at high temperatures (> 800 °C) and considerable expense. A reduction in these requires exploration of chemical deposition carried out in gas or liquid phases. Single Source Chemical Vapour Deposition (SSCVD) effectively delivers a metal organic package of stoichiometric Al:O in the form of aluminium(III) diisopropylcarbamate and reduces the temperature of formation to 500 °C. Amorphous Al(OH)n thin films with an average thickness of 200 nm can also be deposited at even lower temperatures by a simple solvothermal reaction. The decomposition of this carbamate precursor produces hydroxylated thin films at temperature of 65 °C. A subsequently high pressure hydrothermal reaction produces the dehydration of hydroxides and to promote the formation of polycrystalline oxide films. The chemical and structural integrity of these films are examined by XPS and NEXAFS.

The critical feature of these types of fabrication is the control of the thermal stability of the chemical precursor. In particular the selection of precursors which readily undergo β-elimination decomposition pathways and as a result will always produce highly volatile by-products. Resultant films are then always guaranteed to be relatively contaminant free.

4:00pm **TF2-MoA7 Solution Growth of ZnO Nanowires and Thin Films in a Continuous Flow Microreactor**, ***K. McPeak***, *J. Baxter*, Drexel University

Crystal growth from solution is used in the optoelectronic and photovoltaic industries, as well as in the laboratory, for the production of oxide and chalcogenide thin films and nanowire arrays. Chemical bath deposition (CBD) offers advantages over high-temperature vapor phase growth in terms of both cost and compatibility with flexible substrates. However, its widespread use is limited by low process yield and excessive waste solvent, which result because precipitation in solution competes with deposition on the substrate, and also by lack of detailed understanding of how growth conditions impact material properties and morphology. We report on the implementation of a continuous flow microreactor, where the substrate serves as one reactor wall and the chemical bath is contained within a sub-millimeter channel. We have used these microreactors to grow dense arrays of well-aligned single-crystal ZnO nanowires and ZnO thin films. The smaller transport lengths offered by the microreactor design reduce mass transport limitations and mitigate homogenous precipitation, resulting in microreactor deposition yields that can be up to an order of magnitude higher than yields using CBD with conventional reactor geometries. Furthermore, the continuous flow microreactor operates in plug flow, where bath composition changes as a function of position but is time-invariant. Slow flow rates result in nanowires whose lengths, growth mechanisms, and optical properties vary along the length of a single substrate, while fast flow rates produce nanowires that are more uniform across the substrate. Spatially-resolved characterization of the substrate enables rapid and direct correlation of material properties to growth conditions, which is not possible for batch growth where bath composition evolves with time. Here we explore growth at low flow rates to create combinatorial libraries of materials; and we describe the relationship between growth mechanism, strain, and photoluminescence of solution-deposited ZnO nanowire arrays and thin films in unprecedented detail.

4:20pm **TF2-MoA8 Electron Scattering at Single Crystal Cu(001) Surfaces**, ***J.S. Chawla***, *D. Gall*, Rensselaer Polytechnic Institute

We demonstrate specular electron scattering at single crystal Cu(001) surfaces and quantitatively show how Ta and Ta-oxide overlayers, and adsorbed O_2 molecules perturb the periodic surface potential, causing diffuse electron scattering. These findings are an important step towards narrow low-resistivity interconnect wires, and also provide the basis for a new type of gas sensor. Epitaxial Cu(001) layers with thickness d ranging from 20 nm to 1.4 µm were grown on MgO(001) substrates by ultra-high vacuum magnetron sputter deposition at 80 °C. X-ray diffraction θ-2θ scans, ω-rocking curves, and pole figures show the layers are single crystals with a cube-on-cube epitaxy. *In-situ* scanning tunneling microscopy shows 20 to 200 nm wide surface mounds with 0.35 to 0.60 nm wide atomically smooth terraces and atomic level roughness. *In-situ* electron transport measurements at room temperature show a resistivity increase with decreasing thickness, from 1.70±0.06 to 2.65±0.09 µΩ-cm for $d = 1400\pm30$ to 20.0±0.4 nm, respectively. The data is consistent with the Fuchs–Sondheimer model and indicates specular scattering at the Cu-vacuum interface with an average specularity parameter $p = 0.6\pm0.1$. In contrast, layers measured *ex-situ* show completely diffuse surface scattering ($p = 0$) due to sub-monolayer oxidation. Samples that are immersed in liquid N_2 immediately after removal from the vacuum system do not oxidize and exhibit $p = 0.7\pm0.1$ at 77 K. *In-situ* deposition of 0.3 to 7 nm thick Ta barrier layers on Cu(001) films leads to a resistance increase that indicates a transition to completely diffuse surface scattering, independent of the Ta thickness. Oxidation of the Ta layer leads to a partial recovery of the specularity, attributed to a reduced barrier density-of-states at the Fermi-level resulting in a lower scattering probability into barrier-layer states. *In-situ* exposure of Cu(001) layers to partial O_2 pressures P_{ox} between 10^{-8} and 10^{-1} torr cause distinct resistance changes that suggest a multiple step adsorption process: The initially adsorbed O_2 yields a resistance increase due to electronic roughening of the Cu surface, causing complete diffuse scattering at a coverage of 0.14 O_2 monolayers. Continued exposure results in a resistivity drop to the original value, as a complete monolayer is formed that yields specular scattering, followed by an increase associated with diffuse scattering at a chemically oxidized Cu surface. Data analysis provides values for the scattering cross-section of adsorbed molecules and shows that the rate in resistance-change is proportional to P_{ox}, hence, these layers may become useful as thin metal film gas sensors.

4:40pm **TF2-MoA9 Current Fluctuations in Au/HfO$_2$/PT Resistive Switching Memories**, ***C. Vallee***, Joseph Fourier University (UJF) - LTM, France, *P. Gonon,* Joseph Fourier University (UJF), France, *C. Jorel,* LTM, France, *V. Jousseaume*, CEA/LETI, France

In the last years, the semiconductor industry has shown a growing interest for the fabrication of nonvolatile memories based on a resistance switching mechanism to store information: Resistive Random Acces Memories (RRAM). A basic RRAM cell consists in a Metal / Insulating oxide / Metal (MIM) structure where the oxide is a metal oxide (NiO, TiO_2, ZrO_2, Cu_xO…), a perovskite ($BaTiO_3$, $SrTiO_3$…) or a manganite ($Pr_{1-x}Ca_xMnO_3$, $La_{1-x}Sr_xMnO_3$…). A commonly admitted model to explain resistance switching is the formation of conducting filaments upon field-enhanced migration of cations or anions across the film's thickness. In this respect, oxygen vacancies seem to play an important role.

In this work, HfO_2 MIM RRAM cells are elaborated and tested in two electrical modes: voltage sweep mode and constant voltage stress (CVS) mode. The HfO_2 choice is based on the fact that hafnia-based dielectrics are the most promising materials for the manufacturing of CMOS gates below the 45 nm technology node. Therefore, as far as integration and process compatibility are concerned, HfO_2 would be an interesting candidate for the RRAM technology. HfO_2 films (10 nm) were grown at 350°C by atomic layer deposition (ALD) using alternate cycles of H_2O and $HfCl_4$ precursors (1 Torr) on Pt (100 nm) / Ti (10 nm) / Si wafers. The films are crystallized in the monoclinic phase and their gap is around 5.5 eV. Angle-resolved X-ray photoelectron spectroscopy (ARXPS) performed on thinner films (2 nm) reveals a homogeneous composition across the films thickness with a sharp HfO_2/Pt interface (absence of PtO oxides). Top gold electrodes (100 nm thick, 2 mm in diameter) were deposited on the HfO_2 films by dc sputtering.

The voltage sweep mode shows that HfO_2 RRAM is bipolar and that the switching mechanism is probably due to the oxygen vacancies migration and accumulation through the electrical field to the Pt/HfO_2 interface. These positively charged vacancies may act as dopant and form a locally conducive channel in the dielectric. In the CVS mode the device's resistance was observed to be unstable, displaying fluctuations between the high resistance state and the low resistance state which are typical of random telegraph signals. The role played by oxygen vacancies on these fluctuations will be discussed and a mechanism based on a competition between the oxygen vacancies alignment by the electric field and their thermal redistribution by Joule heating will be proposed.

5:00pm **TF2-MoA10 Plasma Beam Deposition of Silver Mirrors**, *J.D. Barrie, C.T. Chu, P.D. Chaffee, C.J. Panetta, K.A. Folgner,* ***P. Fuqua***, The Aerospace Corporation

The high reflectivity of silver coatings in the visible and infrared makes them the mirror of choice for many demanding applications. Unfortunately, these mirrors tend to be affected by exposure to atmospheric contaminants, resulting in corrosion that reduces reflectivity and increases scatter, limiting the mirrors' useful service life. Factors that can affect the stability of silver mirrors include interface adhesion, impurities and pinholes in the dielectric protection layers, and the microstructure and stress levels in the films. This paper examines the preparation of silver mirrors by plasma beam deposition, a relatively new technique for thin film fabrication developed and patented by Plasma Quest, Ltd., and licensed by The Aerospace Corporation. In this method, a high-density inductively-coupled RF-plasma is created external to the deposition chamber, is electromagnetically steered towards a source target, and finally is accelerated towards the target by application of a bias on the target. The separation of plasma generation and transport offers significant advantages in process control. We will present data on how varied deposition conditions, such as plasma beam density and target bias, affect stress and durability of high reflectivity silver mirrors.

Thin Film
Room: B4 - Session TF3-MoA

Energy Applications and Scaling
Moderator: S.M. George, University of Colorado at Boulder

2:00pm **TF3-MoA1 Dye-Sensitized Solar Cells: Fabricating Photoelectrodes via Atomic Layer Deposition**, ***J.T. Hupp***, Northwestern University **INVITED**

Dye-sensitized solar cells (DSSCs) utilize high-area semiconducting metal-oxides as photo-electrodes. The electrodes typically take the form of aggregated nanoparticulate films, supported by planar transparent conducting oxides (TCOs). Depending on the precise composition of the rest of the DSSC, unwanted back electron transfer from the dye-coated electrode to solution-phase (or solid state) redox shuttle can be a major performance-limiting process. We find that atomic layer deposition of insulating alumina or zirconia effectively passivates surface states that mediate the back transfer. Indeed, in some instances a single ALD cycle can slow back electron transfer by as much as four orders of magnitude, with concomitant spectacular improvement in cell photovoltages and fill factors. Alternatively, ALD can be used for photelectrode fabrication. Especially intriguing is the fabrication of quasi-one-dimensional photoelectrodes on high-area anodic alumina oxide or silica aerogel templates. In comparison to conventional 3D nanoparticulate architectures, the 1D electrode architectures offer superior electron transport and shuttle transport behavior. Advanced designs allow for highly efficient radial charge collection, even from inherently transporting materials. The use of ALD to construct these electrodes will be described. If time permits, additional DSSC applications will be described, including ALD-based corrosion inhibition and ALD-based fabrication of cells that employ plasmonic amplification.

2:40pm **TF3-MoA3 Energy Conversion at Nano Scale**, ***F.B. Prinz***, Stanford University **INVITED**

Selective mass and charge transfer drive energy conversion in any living system. Not unlike nature, man-made energy conversion systems such as fuel cells depend on membranes with selective ionic conduction.

Our experiments have shown that we can fabricate freestanding oxide membranes with a thickness of tens of nanometers using Atomic Layer Deposition (ALD). In particular, we used Yttria stabilized Zirconia and Gadolinia doped Ceria as electrolyte membranes for thecreation of a new class Solid Oxide Fuel Cells (SOFCs) which are capable of operating several hundred degrees centigrade below the temperature of traditional SOFCs. First principles calculations help in understanding oxide ion incorporation and ion conductivity as a function of dopant concentration.

ALD promises improved thin films for photovoltaics. Precise depth control of photon absorbing layers allows engineering of bandgaps over a wide range of energy levels. However, high grain boundary density in ALD films may increase exciton recombination rates, thereby reducing conversion efficiency.

3:40pm **TF3-MoA6 Al_2O_3 ALD for Improved Performance of Li Ion Batteries**, ***A.S. Cavanagh***, *Y.S. Jung,* University of Colorado at Boulder, *A.C. Dillon,* National Renewable Energy Laboratory, *M.D. Groner,* ALD NanoSolutions Inc., *S.H. Lee, S.M. George*, University of Colorado at Boulder

Lithium ion batteries (LIBs) are emerging as the dominant power source for portable electronics. Improvement in their capacity lifetime during charge-discharge cycles must be achieved before LIBs can be used for plug-in-hybrid and electric vehicles. $LiCoO_2$ has been the dominant cathode material in LIBs. The instability of $LiCoO_2$ particles comprising the cathodes leads to the deterioration of the LIB. Efforts to stabilize $LiCoO_2$ particles have concentrated on nanometer thick coatings of metal oxides, metal fluorides and metal phosphates deposited using sol-gel techniques. In this study, we demonstrate that Al_2O_3 ALD grown on $LiCoO_2$ particles dramatically enhances their specific discharge capacity.

After coating the $LiCoO_2$ particles with Al_2O_3 ALD in a rotary reactor, battery cathodes were prepared and cycled against a Li/Li^+ anode near the threshold for 50% Li extraction at 1 C-rate after the first two charge-discharge cycles. A control cathode prepared using uncoated $LiCoO_2$ particles was tested for comparison. With respect to the third charge-discharge cycle, the $LiCoO_2$ particles coated with 2 Al_2O_3 ALD cycles showed a 89% capacity retention after 120 charge-discharge cycles. In comparison, the bare $LiCoO_2$ particles displayed only a 45% capacity retention after 120 charge-discharge cycles.

$LiCoO_2$ particles coated with 6 and 10 Al_2O_3 ALD cycles showed lower specific capacities when run at a 1 C-rate after the first two charge-discharge cycles. This lower capacity is attributed to the slower Li^+ diffusion and restricted electron mobility through the insulating Al_2O_3 ALD layer. We propose two mechanisms by which the Al_2O_3 ALD may enhance the cycle performance of the LIBs. The Al_2O_3 film may prevent the $LiCoO_2$ particles from decomposing electrolyte and forming a solid-electrolyte interphase. Alternatively, the Al_2O_3 film may protect the $LiCoO_2$ particles from corrosion by HF.

4:00pm **TF3-MoA7 Impact of Film Thickness and Thermal Treatment on the Excellent Surface Passivation of *c*-Si by ALD Al_2O_3 for Solar Cell Applications**, *G. Dingemans, M.C.M. van de Sanden,* ***W.M.M. Kessels***, Eindhoven University of Technology, the Netherlands

The surface passivation of *c*-Si by atomic layer deposited (ALD) Al_2O_3 has recently gained considerable interest after extremely low surface recombination velocities (< 10 cm/s) have been reported for low resistivity *n*- and *p*-type *c*-Si wafers [1]. The incorporation of an Al_2O_3 film for boron doped emitter passivation led to enhanced efficiencies of 23.2% for *n*-type *c*-Si solar cells [2]. From the cumulative research, various questions related to the thermal stability and other processing aspects of the Al_2O_3 films appeared. In this contribution we will show that a decrease of film thickness down to ~5 nm does not compromise the passivation quality, enabling a straightforward reduction of deposition time and providing freedom in the design of optimal front passivation/antireflection schemes. To activate the Al_2O_3 surface passivation a post-deposition anneal is required, but also the thermal budget during the plasma enhanced chemical vapor deposition of an *a*-SiN_x:H capping layer was found sufficient to activate the passivation. Although an anneal effect can be observed in a large temperature range

(~350 - ~600°C) the optimal post-deposition anneal temperature window was found to be much smaller. Within the optimum temperature range, the largest anneal effect was observed to take place during the first minutes of the process. For the successful implementation of Al_2O_3 in conventional screen printed solar cells, thermal stability is required. In this paper we demonstrate the relative stability of Al_2O_3 and Al_2O_3/*a*-SiN_x:H passivation/antireflection stacks against an industrial "firing" process reaching temperatures > 800°C. Although the minority carrier lifetime was found to decrease during the firing process, values in excess of 1 ms were obtained on 2 Ω cm *n*-Si wafers after firing. These lifetimes suggest that surface recombination will not likely be the efficiency limiting step for solar cells that combine Al_2O_3 passivation and screen printed metallization as recombination in the metalized area will be dominant. The findings in this paper demonstrate the suitability of thin ALD-synthesised Al_2O_3 passivation films for large scale photovoltaic applications.

[1] B. Hoex, J. Schmidt, P. Pohl, M. C. M. van de Sanden, and W. M. M. Kessels, J. Appl. Phys. 104, 044903 2008

[2] J. Bennick, B. Hoex, M.C.M. van de Sanden, W.M.M. Kessels, O. Schultz, S. Glunz, Appl. Phys. Lett. 92, 253504 (2008)

4:20pm **TF3-MoA8 Spatial ALD: Fabrication of Films and Devices at Atmospheric Pressure**, ***D.H. Levy***, *S.F. Nelson, M.S. Burberry, L.W. Tutt, R.S. Kerr, G. Zwadlo*, Eastman Kodak Company **INVITED**

Atomic Layer Deposition (ALD) has proven itself in the fabrication of high-quality films with good uniformity and thickness control. ALD films serve as barriers, surface treatments, dielectrics, and semiconductors. The process has numerous benefits including superior conformality and ease of selective patterning, attributes that make it an ideal tool for upcoming needs in nanofabrication.

To date much of the usefulness of ALD has been demonstrated in enclosed systems where the gases used to effect the deposition are delivered and removed from a chamber in a timed sequence. An alternative to this approach is to keep gas flows of the various reactants at steady state but confined to specific regions of a coating head. Movement of the substrate relative to the coating head yields the required alternating exposure sequence. This method, termed spatial ALD (S-ALD), relies upon methods to isolate closely spaced gas streams. The design approaches to eliminate reactant mixing and to produce good uniformity will be described. Successful gas manipulation has the benefit that not only can reaction gases be isolated from each other, but also these gases can be isolated from the surrounding environment to allow for open-air operation. Because there is no containment chamber and operation occurs at atmospheric pressure, S-ALD is well suited to large and ultimately continuous substrates, such as a moving web.

The use of S-ALD to deposit films onto a range of substrates, both rigid and flexible, as well as webs, will be discussed. The ALD process also allows selective film growth by prepatterning substrates with growth inhibitors. These inhibitors can be applied to flexible substrates with conventional printing techniques. By leveraging selective area deposition, we combine the high quality of ALD films with printing-like patterning, all at atmospheric pressure. This combination is likely a key step in enabling high-quality printed electronics onto flexible substrates.

The performance of films deposited by the S-ALD approach will also be presented, functioning as barriers and components in patterned semiconductor devices. In general, performance of S-ALD films in terms of electrical and physical properties are consistent with the published performance of conventional ALD materials.

5:00pm **TF3-MoA10 Metal Oxide and Fluoride ALD Process Development and Optimisation for Large Area Depositions**, ***M.I. Putkonen***, Beneq Oy, Finland **INVITED**

ALD is a mature technology and globally most of the industrial ALD coating activities are at the moment close to the semiconductors where films are relatively thin. However, there are many industrial areas where substrate sizes can be several square meters and film thicknesses can reach over many micrometers. As a technology ALD does not have issues with thick films. However, the industrial coating system needs to be designed and built for reliable and repeatable processing of thick film stacks. The relative slowness (in nm/h) of ALD can be compensated by optimizing the batch sizes as well as ensure good flow dynamics to obtain fast cycle times. New applications outside semiconductor industry where ALD can possibly be utilized include photovoltaics, diffusion barriers, wear resistant materials and optical coatings aiming to improve competitiveness of existing products and enabling new applications.

Quite often ALD processes are not ideal although films can appear to be uniform at the R&D size substrates. When batch sizes are scaled up to several square meters even small variations in the growth rate or slight thermal decomposition of the precursors can be detrimental. Therefore process tuning is often needed to fix the small deviations of the processes.

In this presentation different approaches to obtain uniform oxide films are discussed in detail. For example, optical thin film stack structures made by ALD there are several possibilities for high index materials but for low index materials the selection is still more limited. Scaling of the processes for batches up to 5-10 m2 of total area is required to obtain reasonable throughput. At the same time the deposition cycle should still be kept a well below 3-5 seconds. For example we have made TiO2 deposition in a large batch consisting of 36 shelves (240x500 mm2) double side coating using Beneq P400 A. Batch uniformity over 8 m2 area was ±2%.

In addition to process optimization to large batches we show preliminary data concerning the deposition of metal fluorides by using novel precursor chemistry based on the traditional metal oxide ALD chemistry using either fluorinated metal β-diketonates or fluorinated hydrocarbons as a fluorine source. According to the RBS film stoichiometry was CaF2.03 with oxygen contamination below the detection limit, i.e. below 5 at.%. The refractive index of films deposited at 300oC was 1.43.

Vacuum Technology
Room: C1 - Session VT-MoA

Pressure, Partial Pressure, and Flow Measurement
Moderator: J. Setina, IMT

2:00pm **VT-MoA1 Investigations on the Dynamic Response of Pirani Gauges**, ***M. Wüest***, *B. Andreaus, R. Stocker*, INFICON, Liechtenstein

For over 100 years the Pirani sensors measure vacuum pressure from ~5x10^{-5} mbar to atmosphere. Pirani sensors are based on heat conduction through gas. Due to this measurement principle the accuracy of Pirani sensors is reduced near atmospheric pressure. Yet many industrial processes use the low cost Pirani sensors for venting applications and the trend is to faster cycle times. Depending on the construction Pirani sensors can display various inaccuracies during rapid pressure changes. This is because the wall temperature measurement used for temperature compensation lags the pressure change. Here we present an investigation to optimize Pirani sensor design for rapid pressure venting applications.

2:20pm **VT-MoA2 Portable Gas Sampling Instrument Capable of Measuring Leak Rates, Volumes, and Pressures without A/C Power**, ***S. Thornberg***, *J. Brown,* Sandia National Laboratories*, L. Miller, J. Ithaca*, B&W Pantex

Certain operations (e.g., volume measurement, gas sampling, and leak rate determination) commonly employed in the field of vacuum technology typically require A/C-powered equipment (vacuum pumps, electrometers, computers, etc.) to perform the measurement or operation. However, some hazardous applications require the cessation of A/C-powered operations when certain conditions exist like the presence of a thunderstorm that can generate dangerous voltage spikes from nearby lightning strikes. To alleviate this problem, a new instrument designed and prototyped at Sandia National Laboratories is capable of performing leak tests (greater than 5 x 10^{-4} atm cc/s air), measuring the internal volumes of complex manifolds (up to liters in volume), making absolute pressure measurements, and performing gas sampling, all without the use of A/C power. The system is designed to be very easy to use with many pneumatic valves behind the instrument panel that are controlled by simple control valves specifically designed/invented for this application. Other functions this instrument can perform are the generation of a modest vacuum (approximately 10 Torr) and backfilling the system with a user-supplied gas. The system has been prototyped, and production models have been fabricated and are in use on production lines. This presentation will highlight the design and features that enable these operations to be performed without A/C power in an operator-friendly package that is not much larger than a thick briefcase. Extensive qualification testing has been performed using these instruments, and the results will be presented to show the performance and NIST traceability. (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.)

2:40pm **VT-MoA3 Mass Spectrometer Sampling of Transient Gas Compositions in Processes**, ***R.E. Ellefson***, Consultant

Many modern vacuum processes involve transient gas densities and compositions. Analysis of the composition of process gas requires the transport of a sample from near the process point of interest to the gas analyzer. The transport time and surface conditioning time of the sampling apparatus needs to be much shorter than the cycle times of the process to give useful composition-versus-time profiles. Many processes for CVD or ALD deposition involve metal organic precursor gases that adsorb on surfaces conformally as part of the deposition process. These gases also adsorb on the sampling system internal surfaces. Management of the surface coverage dynamics for each process is an important factor for good sampling. In this paper, the time constants for species diffusion within the process, sample gas transport and surface coverage times for adsorption and desorption as the composition changes are defined and calculated for typical applications. Strategies for accelerating the stabilization of the sampling system surface composition by controlling surface temperature in relation to the process temperature are discussed. Designs and results for sampling systems and component measurements are presented for four representative processes: Hot He degas of wafers, high-density (fluorocarbon) plasma etch, and monitoring atomic layer deposition and various CVD processes.

3:00pm **VT-MoA4 A Novel Electrostatic Ion Trap Mass Spectrometer**, *A.V. Ermakov*, ***B.J. Hinch***, Rutgers University

We have developed, built and tested a novel mass spectrometer which uses purely electrostatic fields for confinement of in-situ ionized residual gases within a linear trap. An anharmonic trapping potential well focuses the ion trajectories of all ion masses, and of a wide range of ion energies, such that their lifetimes are long enough to allow for systematic sequential ejection of the ion mass/charge ratios. Ions are generated within the ion trap by electron impact of residual gases. Mass selective ejection is achieved through a novel autoresonant pumping process. The mass spectrometer has an unlimited mass range, is capable of achieving high sensitivity at high and ultrahigh vacuum levels, and has demonstrated much faster scan rates than the widely used (larger size and) more complicated quadrupole or magnetic sector mass spectrometers. In addition, the new mass spectrometer is very compact (less than 2" long), and requires very low power (in the mW range, excluding ionizer) as it uses only static bias potentials and a very small RF voltage (in the 100mV range). The principles of autoresonant ejection of ions are presented, along with a detailed analysis of the design and operational parameters affecting mass spectral resolution, detection limit, and dynamic range.

3:40pm **VT-MoA6 A Practical Electrostatic Ion-Trap Sensor**, ***G.A. Brucker***, *J. Rathbone, S. Blouch, M. Schott, K. Van Antwerp*, Brooks Automation, Inc.

We have expanded upon the work of A.V. Ermakov and B.J. Hinch from Rutgers University to further develop a novel electrostatic ion trap sensor that is based upon the principles of autoresonant ion-ejection and detection for use in low mass range mass spectrometry applications. The improved sensor is approximately 15 cm in length, with a 2.5 cm ion-trap component capable of scanning a mass range of 1-300amu with a mass resolving power of >130x. A symmetric RF pumping scheme combined with a custom RF frequency sweep profile provide simplified electrical design along with optimal ion ejection efficiency across the entire mass range. A novel dual-filament, off-axis ionization scheme provides both pressure range and detection limit enhancements. The entire structure that includes the ionizer, mass analyzer and detector were integrated into a pre-existing Stabil-Ion® gauge total pressure ionization sensor envelope. The improved sensor retained many of the benefits of the original concept sensor such as a rapid sensor scanning speed approximately 70ms for 1-100amu scans and a mW RF ion-trap drive requirement that allows for a remote gauge cable connection to the controller electronics. The simple structure and intelligent electronics were implemented to allow for self- calibration of partial pressure measurements and automated recalibration of the electron multiplier detector. A novel dual-filament ionization source design was incorporated into the ion trap to allow fast and easy field replacement of filaments.

4:00pm **VT-MoA7 Total Pressure Measurement Integrated into a Ratiometric Partial Pressure Electrostatic Ion Trap Sensor**, ***P.C. Arnold***, *G.A. Brucker*, Brooks Automation, Inc.

A method of total pressure measurement concomitant with partial pressure analysis in a partial pressure analyzer ion trap will be presented along with representative construction geometries and data of the measurements. This combination of total pressure and partial pressures into a single sensor allows a more complete evaluation of the gas content of a vacuum chamber as well as its changing composition and absolute pressure. This method includes one ionization gauge structure which measures the pump-down progress to evaluate correct time of trap turn-on. Another ionization gauge structure is included that provides total pressure at high vacuum intermittently with the partial pressure scans. Ion traps are ratiometric devices that have an upper limit in the ion density that can be stored in their ionization trapping volumes. This limits the total number of ions measurable so that as pressure increases, no further absolute increase is observed in the sum of the amplitudes of individual gas species peaks, even though the differentiation in the various relative mass peaks continues to be readily seen.

4:20pm **VT-MoA8 Instrument Design for an Integrated Total and Partial Pressure High Speed Vacuum Quality Monitor Sensor**, ***M. Schott***, *J. Rathbone, P. Sandt, K. Van Antwerp*, Brooks Automation Inc.

Design details and performance test results of an integrated total and partial pressure high speed vacuum quality monitor instrument will be presented. A single-sensor, high-speed total pressure and partial pressure instrument has been developed with a 1-100amu, 100ms update rate. The complex sensor is comprised of a hot-filament ion source, electrostatic ion-trap mass separator, Shulz-Phelps based total pressure detector, and an electron multiplier ion detector that is shared for both UHV total pressure and ratiometric partial pressure measurements. A dual board electronics instrument package has been designed to control, drive and process complex sensory data, and output the processed data into a usable form within the cycle time of the measurement update rate. High speed data processing and real time sensor control was achieved by dividing the sensory control and measurement function from the data reduction and host input/output functions. The mass spectrometer interface (MSI) electronics board utilizes a local uC, which directly controls and provides system status on the following sensory functions: multiple ion-trap bias voltages, filament power & emission current, ion-trap mass analyzer RF drive amplitude & frequency and ion current electrometers. The MSI local processor accepts serial high-level commands from the host input/output (HIO) board processor, which predetermines the sensory "scan" control parameters. The HIO board performs data reduction and user input/output. HIO data reduction algorithms process the raw sensory data into usable total and partial pressure [amu, amplitude] matrix data. All resulting in hard-coded and/or custom user outputs, which may produce a number of real-time and non-real-time datum.

4:40pm **VT-MoA9 NIST Traceable Vacuum Standard Based upon MEMS Resonant Silicon Gauge Technology**, ***J. Hendricks***, *T. Gooding, D.A. Olson*, National Institute of Standards and Technology

In the mid 1990's the development and use of micro electro mechanical systems (MEMS) enabled pressure sensor technology to make significant advances in both precision and accuracy. Resonant Silicon Gauges (RSGs) are MEMS sensors that are manufactured by micromachining silicon to produce silicon diaphragms nominally a few millimeters square by a fraction of a millimeter thick. Over the past decade, NIST has calibrated these gauges and has found them to be very stable, rugged, and ideally suited as core technology for a high-stability precision pressure standard that can be calibrated against the NIST primary pressure standards [1].

The RSGs use two single-crystal silicon resonators encapsulated in a vacuum microcavity. Changes in pressure on the diaphragm are determined by measuring strain-induced changes in the two resonant frequencies [2]. Since each resonant element is encapsulated in a vacuum, the most critical part of the sensor is never in direct contact with the calibration gas which makes the pressure sensor gas species independent. The RSG sensors are commercially available and NIST has performance data dating back over 9 years on one sensor that has been calibrated 18 times, and has a demonstrated average calibration shift of only 0.008% [3].

NIST has developed and built a Resonant Silicon Gauge Transfer Standard Package (RSG-TSP) with a range of 100 Pa to 130 kPa. NIST scientists recently completed a long-term stability study of this transfer standard, demonstrating that the uncertainty due to stability is only a few ppm at 130 kPa, increasing to 0.01 % at 100 Pa (k=1). This standard is expected to find applications in national "round robin" and international key comparisons of pressure standards, and is ideally suited for use as a "high end" precision pressure standard for secondary calibration laboratories.

[1] Hendricks, J.H. et.al. Metrologia 44 (2007) 171-176.

[2] Harada, K. et.al. 1999 Sensors and Actuators 73 261-266.

[3] NIST internal calibration report NC212.

5:00pm **VT-MoA10 A New Approach to Gas Flow Calibration**, ***P.D. Levine***, Zero K Designs

Gas flow calibration is typically accomplished by measuring the rate at which volume is displaced by gas flowing at constant pressure. The measurement relies upon the accurate determination of the first order change in position of the object displacing the gas. Through active control of gas pressure and displacement, higher order effects are minimized to enhance measurement precision. These systems are mechanical in nature and require substantial sophistication in their manufacture and utilization to achieve primary standards levels of uncertainty. An alternative method which generates volumetric flow-rates by non-mechanical means is described. The method takes advantage of a natural physical process inherently linear to first order within practical measurement intervals.

By allowing gas to leak from a fixed volume through a throttling valve, leak-down can be controlled such that first order effects dominate for measurement times sufficient for high precision data to be obtained. The volumetric flow-rate is directly proportional to the rate of pressure drop within the fixed volume during the measurement interval. Thus accurate measurements of the fixed volume and the rate of pressure drop can yield high precison results. This method takes full advantage of the resolution and sensitivity offered by state of the art Capacitance Diaphragm Gages (CDG) as used in national standards laboratories. As such, it should be possible to achieve uncertainty levels approaching those of primary references. Indeed, previous work has proven this method as effective as displacement based standards for orifice flow calibration systems[i] . The basic concept lends itself to many realizations making it capable of covering a wide range of flow rates.

One such realization, which can be readily assembled from off the shelf components and some custom fabrication of flow manifolds, is described. It would be capable of providing calibration to 1000 SCCM (Standard Cubic Centimeters per Minute) with a minimum estimated *k*=2 uncertainty of 0.60%.

The Precision Gas Flow Calibrator described here represents a new and simplified approach to gas flow calibration. The achievable measurement precision offers the potential of a stable and reproducible reference with great utility for the calibration of a wide variety of gas flow measuring devices.

[i] P.D. Levine, J.R. Sweda, "A Precision Gas Flowmeter For Vacuum Calibration", J. Vac. Sci. and Technol. A 15(3) May/June 1997; pp 747-752.

Applied Surface Science
Room: C2 - Session AS+EM+MS+TF-TuM

Spectroscopic Ellipsometry III
Moderator: M. Schubert, University of Nebraska - Lincoln

8:00am **AS+EM+MS+TF-TuM1 Optical Characterization of Plasma-Deposited SiO_2-like Layers on Anisotropic Polymeric Substrates**, ***G. Aresta***, Eindhoven Univ. of Tech., The Netherlands, *A.P. Premkumar,* Materials Innovation Inst. (M2i), The Netherlands, *S.A. Starostin,* Eindhoven Univ. of Tech., The Netherlands, *H. de Vries,* FUJIFILM Mfg Europe B.V, The Netherlands, *M.C.M. van de Sanden, M. Creatore*, Eindhoven Univ. of Tech., The Netherlands

Amongst the most common thin film characterization tools, spectroscopic ellipsometry (SE) is increasingly used to determine the layer optical properties. Such characterization is still a challenge when optical anisotropy is present either in the film or in the substrate. The study of thin films deposited on polymeric substrates is an example because polymers often show optical anisotropy. In this contribution the optical characterization of poly(ethylene 2,6-naphtalate) (PEN) in its transparent region is carried out by means of Transmission Generalized Ellipsometry (TGE) and reflection multi- angle SE measurements. TGE measurements allow the determination of the in-plane and out-of-plane anisotropy and orientation of the material index ellipsoid, with respect to the laboratory frame. Reflection multi-angle SE measurements are performed to determine the absolute refractive index values along the x, y and z directions (i.e. the laboratory frame). The full optical characterization of PEN substrates has been carried out first by identifying its in plane anisotropy (i.e. $\Delta n_{xy} = n_y - n_x$) and in-plane orientation of the material index ellipsoid with respect to the x axis, by means of TGE measurements at 0° angle of incidence. A second step consisting of TGE measurements at different angles of incidence has allowed the determination of the out-of-plane anisotropy (i.e. $\Delta n_{xz} = n_x - n_z$) and the material index ellipsoid out-of-plane orientation with respect to the z axis. Finally, reflection multi angle measurements have allowed the determination of the optical dispersions along the three axes (x, y, z). The values of the refractive index calculated at 633 nm are $n_x = 1.74$, $n_y = 1.75$ and $n_z = 1.52$. This characterization is functional to the determination of the refractive index of plasma-deposited SiO_2-*like* layers deposited on PEN substrates. The SiO_2-like samples have been deposited in Atmospheric Pressure Glow discharges [1,2] from Ar/O_2/hexamethyldisiloxane mixtures at different duty cycles. SE measurements have been performed in ambient air and *in vacuum*: an increase of the refractive index values with the duty cycle has been observed, attributed, on the basis of complementary diagnostics, to an increase in film density with the duty cycle.

References:

[1] S. Starostine, E. Aldea, H. de Vries, M. Creatore, M. C. M. van de Sanden Plasma

Process. Polym. 4, S440–S444 (2007)

[2] S. A. Starostin, M.A. M. El Sabbagh, E. Aldea, H. de Vries, M. Creatore, and M. C. M. van de Sanden

IEEE transactions on Plasam Science, 36, 4, (2008)

8:20am **AS+EM+MS+TF-TuM2 Spectroscopic Ellipsometry in the Mid IR and UV-VIS for Investigating Low Temperature Plasma Activated Wafer Bonding**, *T. Plach,* ***K. Hingerl***, University Linz, Austria, *V. Dragoi, M. Wimplinger*, EV Group, Austria

Low temperature plasma activated direct wafer bonding (LTPADWB) for Si-SiO_2 interfaces is a process that lowers the required annealing temperatures, (from usually 900°c down to 250°C) necessary for reaching high bond strength. The mechanism behind this improvement is still under discussion: The low temperature steps for the hydrophilic process are interpreted as follows: Up to 100°C the substrate surfaces are held together via van der Waals interaction which is mediated by a few monolayers of water. In the range of 100-200°C the water diffuses away from the interface both along the interface and through the oxide into the crystalline bulk, where it reacts with the silicon and forms oxide. The remaining half of the bond strength is usually attributed to a closing of gaps at the interface[1], which starts with conventional techniques at the softening temperature of the thermal oxide at around 850-900°C.

In comparison the same surface energies for the LTPADWB process are already reached at 250°C. To clarify the mechanism for this process, different bonding experiments were performed to evaluate the lifetime of the surface activation and the achievable bond strength when using substrates with various orientations. By covering half of the wafer during plasma activation, comparisons between the activated and non-activated region could be made by mid IR and UV-VIS spectroscopic ellipsometry covering the energy range from phonon energies to the UV (30meV-6.5eV). it turns out that the spectral shape of the phonon peaks as well as the spectral shape of the critical points in the UV (E_1, E_2) significantly change and even the peak position changes.

Correlation measurements, by Auger analysis and by X-ray photoelectron spectroscopy.Interfaces of bonded wafer pairs have been performed in addition, as well as by transmission electron microscopy (TEM). TEM clearly shows that there is no discernible interface between the native oxide on one side and the thermal oxide on the other side.

From the spectroscopic ellipsometry data it was found that the top surface stoichiometry is chemically changed, which favors bonding. Finally a model for the mechanism that explains the experimental results will be presented.[1] Q.-Y. Tong, U. Gösele, Semiconductor Wafer Bonding: Science and Technology, Wiley

8:40am **AS+EM+MS+TF-TuM3 Applications of Ellipsometry and Polarimetry to Real-Time Analysis and Control of Epitaxial Growth**, ***D.E. Aspnes***, North Carolina State University and Kyung Hee University, Korea **INVITED**

Many aspects of epitaxial growth are now mainstream technologies, routine enough so that real-time monitoring simply gets in the way. However, the situation is different in emerging areas involving the heteroepitaxy of chemically or lattice-mismatched materials, where paths to success through kinetics and thermodynamics are not well understood, or even identified. Here, real-time analysis and control by ellipsometry or polarimetry not only can provide unique information but may also be essential in achieving objectives. In particular, these techniques can provide information about the critical initial stages of growth well down into the submonolayer scale in addition to the evolution of growth beyond the first monolayer. Further, analysis of data records allows diagnostics to be performed after the fact, permitting detailed analyses of processes that went wrong -- or right. I provide examples from our experiences with organometallic chemical vapor deposition, including sample-driven feedback-control of composition and the analysis of the initial phases of epitaxy of such diverse systems of GaSb on GaAs, GaP on Si, and ZnO on sapphire. The latter application involves a material whose precursors react in the gas phase and where the product sublimes. Real-time polarimetric data provided the information needed to grow high quality material.

9:20am **AS+EM+MS+TF-TuM5 Spectroscopic Ellipsometric Sudy of Phase-Change Materials for Data Storage Applications**, ***E. Gourvest***, STMicroelectronics, France, *C. Vallée,* LTM - CNRS/UJF/INPG, France, *S. Lhostis,* STMicroelectronics, France, *Ch. Licitra, A. Roule,* CEA - LETI, France, *B. Pelissier,* LTM - CNRS/UJF/INPG, France, *S. Maitrejean*, CEA - LETI, France

Chalcogenide materials are widely used for phase change data storage based on the remarkable change of properties between the crystalline and the amorphous phase. The fast and reversible phase transition is accompanied by a high electrical and optical contrast and consequently a change of electronic structure which is still not well understood. In this work we present the optical function spectra of different phase-change materials. $Ge_2Sb_2Te_5$, Ge-doped GeTe and N-doped GeTe films were grown by co-sputtering PVD method on 200 mm wafers and were treated with different annealing temperatures. Film thickness, oxydation and composition were evaluated using X-Ray Reflectivity, Rutherford BackScattering and Angle Resolved XPS.

Optical parameters were fitted from data measured by variable angle spectroscopic ellipsometry. Measurements were carried out between 0.5 and 8 eV for $Ge_2Sb_2Te_5$ samples in amorphous, fcc and hc crystalline phases in order to characterize phase-change bulk layer and surface oxide layer. Ge doped GeTe and N-doped GeTe samples were measured between 0.6 and 6 eV for amorphous and rhombohedral phases.

Ge, Sb and Te thin films are also elaborated by PVD in order to obtain optical laws for the different elements and well defined the optical response of their oxides. Then, optical responses of GST, Ge-doped GeTe and N-doped GeTe films are simulated using Tauc Lorentz law and including the presence of the oxidized upper layer identified by XPS and XRR. Finally, Ge-rich GeTe films before and after crystallization are analyzed using Tauc Lorentz law as well as BEMA. Influence of Ge and N doping in GeTe optical properties (in terms of gap and refractive index) is then discussed. The comparison between as-deposited samples and annealed samples shows in some case the presence of Ge phases in a GeTe medium.

9:40am **AS+EM+MS+TF-TuM6 VUV Optical Properties of III-Nitrides in the Thin Film Limit**, ***C. Cobet***, *M. Röppischer, C. Werner,* Institute for Analytical Sciences, Germany, *R. Goldhahn,* Ilmenau University of Technology, Germany, *N. Esser*, Institute for Analytical Sciences, Germany

In the last few years no other class of semiconductors has attracted so much scientific and simultaneously commercial attention like the group III-nitrides. The extraordinary physical properties have stimulated many new developments of (opto-)electronic devices. Prominent examples are the short wavelength laser diodes, which take advantage of the wide band gap of GaN (3.42eV). Such devices consist of three compounds: InN, GaN, AlN and their ternary or quaternary alloys. The respective band gap shifts from the near infrared for pure InN (0.68eV) to the ultraviolet for AlN (6.03eV), while the lattice constant variation is relatively small and allows the growth of heterostructures. It is probably surprising that several fundamental physical properties are still under discussion, although the III-nitrides are already widely used. Uncertainties concern, for example, the question whether zinc blende AlN has an indirect band gap or the impact of electric fields and strain on the electronic band structure. The latter effects are significant in particular for thin films, quantum wells, and super lattice structures. Furthermore, quantum size effectsalter the optical properties of such structures. But, also the knowledge about the bulk optical properties above the fundamental band gap is still incomplete.

We apply broad band spectroscopic ellipsometry from the visible to the vacuum ultraviolet. It is an excellent method in order to study electronic band structure peculiarities by means of dipole transition features in the dielectric function. On the other hand, it also allows a very precise determination of the dielectric function itself (refractive index and absorption). Device performance critically depends on the optical properties around e.g. the emission wavelength. However, this spectral region is strongly influenced by all higher inter band transitions according to the Lyddane-Sachs-Teller relation. For our investigations on binary GaN and AlN, as well as on ternary $Al_xGa_{1-x}N$, we have mainly used a home made synchrotron ellipsometer. The extraordinary properties of the synchrotron light source allow measurements with very high spectral and spatial resolution in a very broad spectral range. By taking advantage of the polarization sensitivity, we could determine the independent ordinary and extraordinary dielectric function in the hexagonal materials. In a comprehensive discussion of the dielectric functions for the hexagonal and cubic crystal structure, we could identify band gap related excitons and all higher interband transitions. This knowledge is used in order to study effects of composition and strain, as well as quantum size effects in more detail.

10:40am **AS+EM+MS+TF-TuM9 Parameterization of the Optical Function of Hydrogenated Amorphous Carbon by Means of B-splines**, ***J.W. Weber***, *T.A.R. Hansen, M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, The Netherlands

Spectroscopic ellipsometry (SE) is a non-invasive optical diagnostic that measures the change in polarization of light reflected on a thin film. To extract both the optical function and thickness of the film from SE data, a (multi-layered) model is required that describes the interaction of the incident light with the film. For amorphous materials this interaction is commonly modeled by the Tauc-Lorentz oscillator and is used to parameterize the optical function [1].

However, a fully mathematical Kramers-Kronig consistent description of the optical function by means of B-splines is also possible [2]. The B-spline parameterization requires no pre-existing knowledge about the interaction of light with the film. The layer structure for this model consists of a substrate, the bulk layer, of which the optical function is represented by B-splines, and a roughness layer. The roughness is modeled by an effective medium approximation of 50% bulk material and 50% voids. This layer structure is verified by cross-sectional scanning electron microscopy (SEM) measurements. The roughness is in good agreement with values determined by atomic force microscopy (AFM).

When the B-spline model is applied to SE data obtained during growth, it has been found that the optical function for every measured thickness is the same, thereby ascertaining the homogeneity of the bulk layer of the *a*-C:H. During etching of *a*-C:H with a hydrogen plasma, the optical function of the film - due to the homogeneity of the bulk material - can be fixed throughout the entire etch process, which enables real time *in situ* monitoring of the thickness evolution.

Further parameterization of the dielectric function, as found by the B-spline model, by a physics-based model is possible. For *a*-C:H films, the bulk layer is described by two Tauc-Lorentz oscillators, from which the sp^2/sp^3 ratio has been, tentatively, determined from SE data up to 6.5 eV [3].

In all, the B-spline model is an accurate and fast method to determine thickness, roughness and optical constants for numerous types of thin films, including - as has been shown - hydrogenated amorphous carbon. The determined film properties can also be used as input parameters for physics-based models.

[1] G.E. Jellison and F.A. Modine Appl. Phys. Lett.69 (1996) 371

[2] B. Johs and J.S. Hale, Phys. Stat. Sol. A **205** (2008) 715

[3] S. Kassavetis et al., Diamond Relat. Mater.16 (2007) 1813

11:00am **AS+EM+MS+TF-TuM10 Characterization of P3HT Anisotropic Thin Films with Spectroscopic Ellipsometry**, ***J.N. Hilfiker***, *J. Sun, T.E. Tiwald, G.K. Pribil*, J.A. Woollam Co., Inc.

Many methods have been developed to enhance the information content from spectroscopic ellipsometry (SE) measurements. This has allowed precise characterization of dielectrics, semiconductors, and even thin metal films. Appropriate strategies for SE characterization are needed as the thin films become more complex. The thickness and index of transparent films are readily determined. Absorbing films require additional information to uniquely determine thickness and complex refractive index. SE methods for absorbing films include interference enhancement, multi-sample analysis, optical constant parameterization, and simultaneous analysis of SE and intensity-based optical measurements.

P3HT is both absorbing across the visible spectrum and anisotropic. The anisotropy is due to molecular stacking and results in a difference between the complex refractive index parallel to the surface (in-plane) and normal to the surface (out-of-plane). To precisely characterize P3HT films requires determination of film thickness and both in-plane and out-of-plane complex refractive indices. The methods developed for absorbing films are applied to a series of P3HT thin films prepared with multiple thicknesses and on multiple substrate types.

Thick SiO_2 coatings on silicon provide interference enhancement which modifies the light-interaction in the P3HT layer as angle of incidence changes. Characterization is compared with different underlying SiO_2 thicknesses. Multi-sample analysis increases measurement information by combined analysis of samples with a common set of P3HT optical constants. This is applied to P3HT films with different thickness, as well as films coated on different substrates. The combination of SE and intensity-based measurements provides additional information about absorbing films. For P3HT coatings on glass, normal incidence transmittance can provide additional sensitivity to the in-plane complex refractive index. Optical constant parameterization reduces the solution-space, commonly restricting the optical constant functions to be smooth, continuous and Kramers-Kronig consistent. These methods are compared for P3HT films with a discussion of both merits and limitations.

11:20am **AS+EM+MS+TF-TuM11 Analysis of CdTe and CdS Thin Films and Photovoltaic Device Structures by Spectroscopic Ellipsometry**, ***M.N. Sestak***, *J. Li, J. Chen, C. Thornberry, D. Attygalle, R.W. Collins*, University of Toledo

The techniques of in-situ real-time and ex-situ spectroscopic ellipsometry (SE) have been applied for the analysis of polycrystalline II-VI thin films and device structures fabricated by magnetron sputtering onto various substrates for photovoltaics (PV) applications. The CdS/CdTe heterojunction PV technology has led to efficiencies as high as 14% (for an all-sputtered device), and to the lowest module manufacturing costs in the PV industry (< $1/W). In our SE studies, depositions of individual CdTe, CdS, and $CdTe_{1-x}S_x$ films on smooth crystalline silicon substrates have provided information on the nature of thin film nucleation and coalescence, as well as on the evolution of the dielectric function with thickness and quantum size effects in very thin films (< 30 nm). Films remain sufficiently smooth to a thickness of ~ 50 nm under a wide range of deposition conditions so that accurate dielectric functions could be determined as a function of temperature upon suspending the deposition at this thickness and cooling the film to room temperature. Such dielectric functions are deemed accurate because they are measured in situ under high vacuum, thus avoiding surface oxidation and contamination. In addition, surface roughness corrections are made based on roughness determinations obtained from the full real time SE data set. Variations with deposition conditions in the critical point parameters of the resulting room temperature CdTe and CdS dielectric functions have provided information on film stress, defects, and grain size. Upon reheating the film to the deposition temperature and resuming the deposition for the fabrication of the thick (~ 1 micron) films used in PV devices, surface roughness evolution and void volume fraction depth profiles have been extracted. These provide key insights into the optimization of a subsequent CdTe processing step – an anneal in $CdCl_2$ vapor which promotes grain growth and strain relaxation in the active CdTe layer for high efficiency PV devices. Ex situ ellipsometry techniques have also been developed that involve smoothening the thick CdTe film with a succession of $Br+CH_3OH$ treatments that enables step-by-step etching and time reversed spectroscopic ellipsometry on $CdCl_2$ treated device structures. Finally, through-the-glass SE has been developed for multilayer analysis of completed PV devices with the potential for scale up to full 2' x 4' modules in a mapping mode using the reference dielectric function database developed by real time SE.

11:40am **AS+EM+MS+TF-TuM12 Synergism of Ellipsometric Porosimetry with Other Complementary Characterization Techniques for Process Control of Ultra Low k Dielectric Films***, **A. Madan**, N. Klymko,* IBM*, D. Kioussis,* GLOBALFOUNDRIES*, G. Dubois, L. Tai, M. Chace, D. Restaino, J. Protzman*, IBM

This paper discusses new protocols established for matching material properties of ultra low k films for tool matching and process control required for robust manufacturability. These are based on extensive repeat off-line measurement of 2 different films to determine the precision (3 sigma variation), reproducibility and error bars in the measurements.

At the 45 nm node, porosity was first introduced into the interconnect structures in the form of porous SiCOH (pSiCOH) inter-level dielectric films to reduce the capacitance-resistance delay. pSiCOH films are typically deposited using Plasma Enhanced Chemical Vapor Deposition (PECVD) when a precursor containing C, H, Si, O and a hydrocarbon porogen precursor are simultaneously introduced in the processing chamber and RF power is applied. Subsequent exposure to UV irradiation results in the removal of porogen (CHx phase) to create porosity and therefore a lower k value.

Optimization of the UV cure time of the film is critical since overcuring of the film can result in unwanted demethylation and extended network crosslinking of the siloxane backbone which can collapse the pores, altering the porosity, and detrimentally increasing the k value. In-line ellipsometric measurements of refractive index and shrinkage are typically used to monitor the film properties and do not completely reflect the changes in the porosity.

This paper will discuss the methodology for the quantification of the % porosity using Ellipsometry Porosimetry(EP). In addition, measurements of carbon content using XPS, remnant porogen using thermal gravimetric analysis (TGA), and demethylation using FTIR will be presented and correlated to the % porosity. For a 5000A pSiCOH film with 25% porosity, repeatibility studies using off-line EP measurements showed 0.5% variation. Composition from XPS sputter depth profiling resulted in C: 16.0 +/- 4.0 at%; Si: 38.0 +/- 4.0 at%, and O: 46.0 +/- 4.0 at%. The FTIR CH2 peak at 2885 cm-1 normalized to SiOSi peak <0.070 mAU (milliAbsorbance Units) was determined to be an appropriate measure of the porogen removal, along with porogen weight loss in the cured film at 1.0+/-0.5% using TGA. The FTIR methyl silicon CH3 peak at 2974cm-1 at 0.0125 +/- 0.0006 AU (normalized to SiOSi peak) is a sensitive parameter indicative of an overcured condition. Cross linking criteria could not be reliability established, though degree of crosslinking is related to changes in the bulk modulus observed with various cure conditions.

The end result is a more comprehensive and accurate characterization of the ultra low k pSiCOH films, thereby ensuring needed manufacturing controls for chamber matching and tool qualification.

Biomaterial Interfaces
Room: K - Session BI-TuM

Proteins and Cell Interactions at Interfaces II
Moderator: H.E. Canavan, University of New Mexico, S.L. McArthur, Swinburne University of Technology, Australia

8:00am **BI-TuM1 Molecular Simulation as a Surface Design Tool to Understand and Control Protein-Surface Interactions***, **R.A. Latour***, Clemson University **INVITED**

Protein-surface interactions are of great importance in a wide variety of applications in biomedical engineering and biotechnology, including medical implants, biocatalysis, immobilized-enzyme bioreactors, biosensors, bioseparations, and bioanalytical systems. While this is well recognized, very little is understood regarding how to design surfaces to optimally control protein adsorption behavior. To address this limitation, we are working on the development of molecular simulation methods to accurately predict protein-surface interactions at the atomic level. We have found that this type of molecular system is sufficiently unique that molecular simulation methods cannot simply be borrowed from other applications; but rather, they must be critically evaluated and often modified to accurately represent adsorption behavior. In this talk, I will address four major areas that we have identified as being particularly important for the simulation of protein-surface interactions, and I will present our approaches to address each of these areas. These are (1) the general methods that are needed to properly simulate protein-surface interactions, (2) the suitability of a force field to represent protein-surface interactions, (3) the adequate treatment of solvation effects, and (4) the need for advanced sampling methods for large molecular systems. I will present an overview of our efforts to address each of these key areas. We are developing a hybrid force field program that enables multiple force fields to be used in a single simulation to represent different phases of a system (e.g., solid surface, solution, and the interphase between them), methods to enable pressure to be properly monitored and controlled in a simulation with constrained atoms, and how electrostatic effects should be represented for surfaces with high charge density when using periodic boundary conditions. We have generated a large experimental benchmark data set for peptide-surface interactions for use for force field evaluation, modification, and validation purposes along with simulation methods to calculate adsorption free energy for comparison with this data set. Regarding solvation effects, we have found that existing implicit solvation methods are completely unsatisfactory at this time and must be redeveloped before use in protein adsorption simulations. Finally, we are also developing advanced sampling methods for large molecular systems to efficiently overcome energy barriers that often cause simulations to become trapped in local low-energy states and prevent proper exploration of the relevant phase space of the molecular system.

8:40am **BI-TuM3 Surface-Induced Changes in the Structure of Beta-Helical Peptides***, **K. Fears**, J. Kulp III, D.Y. Petrovykh, T. Clark*, US Naval Research Laboratory

The stable structure of beta-helical peptides in solution provides a well-defined starting point for discerning the changes in secondary structure of peptides induced by surface adsorption. Understanding the adsorption of proteins on surfaces is of critical importance in medical- and bio-technology. The determination of the secondary and higher-order structure of adsorbed proteins, however, is challenging due to their inherent complexity. Peptides with simple secondary structures provide a good model for investigating the interactions between surfaces and the structural subunits of proteins. Beta-helical, rather than alpha-helical, peptides were selected for this study because of their stability and tendency to maintain a monomeric, unaggregated structure. Peptides were custom designed to switch between two different stable conformations as a function of solvent composition, as confirmed by nuclear magnetic resonance (NMR) and circular dichroism (CD) spectroscopies in solution. These peptides were adsorbed onto silica substrates from aqueous and organic solvents to determine their conformation post-adsorption. The secondary structure assignments of the adsorbed peptides were based on the comparison of their CD spectra to spectra of the same peptides in their known solution conformation. Our ability to measure the secondary structure of peptides that are adsorbed as monolayers on planar substrates suggests that CD spectroscopy can be used to gain insight about the adsorption behavior of individual subunits that provide support and/or functionality to proteins.

9:00am **BI-TuM4 Enantiospecific Adsorption of Serine Enantiomers on the Chiral Cu{531} Surface***, T. Eralp, A. Shavorskiy,* University of Reading, UK*, D. Batchelor,* BESSY and Universität Würzburg, Germany*,* ***G. Held***, University of Reading, UK

The production of enantiopure chiral bio-relevant molecules is of significant importance for the development of new pharmaceuticals and the improvement of existing ones. In this context chiral surface systems, e.g. chiral molecules adsorbed on chiral single crystal surfaces, are of considerable interest as they are model systems for potential enentioselective heterogeneous catalysts or enantiomeric selection. In this study the adsorption properties of L- and D- Serine enantiomers on the intrinsically chiral Cu{531} surface were investigated. These aminoacids have four functional groups which can make bonds to the Cu{531} surface: OH, NH_2, and two oxygen atoms in the carboxyl group (-COOH). The geometry of the adsorption complex was characterised using XPS and NEXAFS. The bonding characteristics of the molecule strongly depend on the coverage. The main peak in the O1s XPS spectra, at BE 531.5eV, is assigned to be overlapping signal of the two oxygen atoms in the deprotonated carboxylate (COO) group forming bonds with Cu atoms. For the low coverages this peak has a shoulder at a lower BE (530.7 eV), as the coverage increases this shoulder disappears and a new peak appears at higher BE (532.8 eV). The low BE shoulder at low coverage is assigned to the OH group also forming a bond with the Cu surface. With increasing coverage the surface becomes more crowded and a less space-consuming configuration is assumed with a 'dangling' OH group, which is the origin of the high BE O1s peak.

In order to investigate the orientation of the amino acids within the surface NEXAFS spectra were recorded for different in-plane polarization angles and different coverages. These spectra show large enantiomeric differences between the orientation of D-serine and L-serine, which is also reflected in the LEED patterns, indicating different long-range ordered overlayers. These enantiomeric differences are much bigger than those previously observed for alanine on the same surface, which suggests that the size and the nature of the amino acid side group is the dominating factor for enantioselective behaviour on this surface.

9:20am **BI-TuM5 Investigation of Surface-Bound Protein Conformation/Orientation Using Time-of-Flight Secondary Ion Mass Spectrometry**, ***L.J. Gamble***, *F. Cheng, J. Brison, L. Árnadóttir, D.G. Castner*, University of Washington

The adsorption of protein to solid surfaces is typically accompanied by structural rearrangements as well as loss of bioactivity. These changes can be monitored by time-of-flight secondary ion mass spectrometry (ToF-SIMS) and the protein activity monitored by surface plasmon resonance (SPR). However, the ultra-high vacuum of the ToF-SIMS can alter the protein conformation. In this study ToF-SIMS was coupled with a variable temperature sample stage to monitor the conformational changes that occur when a surface-bound protein goes from a hydrated to a dehydrated state. Changes in bioactivity of the surface bound proteins were investigated using SPR. Initial ToF-SIMS and SPR experiments were conducted on a surface-bound protein system of histagged humanized anti-lysozyme variable fragment (HuLys Fv) coordinated on a Ni^{2+}-loaded nitrilotriacetic acid (NTA) surface. Continuing studies investigate fibrinogen (and fibrinogen fragments). Positive ToF-SIMS data from the protein surfaces were acquired with an ION-TOF TOF.SIMS 5-100 system (ION-TOF GmbH, Münster, Germany) . Applying principal component analysis (PCA) to the ToF-SIMS data, the spectral differences resulting from two surface coverages and various heat treatments were determined. The spectra are separated into three groups: high protein coverage samples, low coverage below -80ºC, and low coverage at -60ºC and above. Trends observed in the plot suggest both surface coverage and heat treatment affected the secondary ion spectra. At the temperature below about -80oC, the protein molecules are frozen into their hydrated conformation. As the temperature is raised changes expose hydrophobic amino acid residues. The antigen binding capacity of surface-bound HuLys Fv before and after dehydration was measured by SPR. At the low coverage, the antigen binding capacity on the dried protein film was roughly 50% lower than that on the fresh film. As comparison, high coverage dried samples lost ~20% binding capacity. The loss of HuLys Fv bioactivity on the dried protein film was attributed to an irreversible disruption of protein native conformation during the drying process. The high coverage samples exhibited less loss of bioactivity, consistent with the smaller conformational changes observed by PCA. The use of the sugar trehalose as a protein stabilizer is also investigated.

9:40am **BI-TuM6 Soft X-ray Spectromicroscopy of Protein Interactions with Model Biomaterials**, ***B.O. Leung***, *A.P. Hitchcock, J.L. Brash,* McMaster University, Canada*, A. Scholl, A. Doran*, Advanced Light Source

Upon implantation in biological tissue or first contact with blood, all materials are immediately coated with a layer of proteins. The details of this initial protein layer can have a very strong effect on biocompatibility [1]. Thus, characterization of the surfaces of biomaterials and their interaction with relevant proteins can help to determine and understand biocompatibility.

We use synchrotron based X-ray photoemission electron microscopy (X-PEEM) [2] and scanning transmission X-ray microscopy (STXM) [3] to study the spatial distribution of adsorbed proteins on chemically heterogeneous surfaces. Both techniques have a lateral spatial resolution below 40 nm, provide speciation and quantitation through spatially resolved near-edge X-ray absorption fine structure (NEXAFS) spectroscopy, and can be used to obtain quantitative maps of the adsorbed protein in relation to the topography and chemistry of the underlying substrate with high sensitivity [4-5]. X-PEEM probes the top 10 nm of the sample whereas STXM integrates over the full sample thickness (40-100 nm) and can be applied to fully hydrated samples.

Results from three recent studies will be presented. (1) spun-cast thin films of phase-segregated polystyrene blended with cross-linked polyethylene oxide (PEO) adsorb human serum albumin (HSA) more readily to the PEO -rich areas compared to plasma-deposited diglyme surfaces, which are known protein resistant materials. Due to incomplete phase segregation, PEO imparts some protein resistance to the PS region. (2) HSA adsorption to polystyrene/ poly(methyl methacrylate)-b-polyacrylic acid (PS/PMMA-b-PAA) thin films show strong modifications of the adsorption behavior relative to HSA adsorption to PS/PMMA surfaces due to strong and specific electrostatic interactions between the positively charged peptide and the negatively charged PMMA-b-PAA domains. (3) Protein adsorption to PS-PMMA spun-cast films has been examined by STXM in a fully hydrated wet cell. In the presence of water, HSA preferentially adsorbs to the discrete polar PMMA domains rather than the continuous PS domain, whereas the latter is favored under dried conditions [2]. [6]

1. D. G. Castner, and B. D. Ratner, *Surface Science* **2002**, *500*, 28 – 60.

2. L.Li, J. Brash, R. Cornelius and A. P. Hitchcock *J. Phys. Chem B* **2008,** *112*, 2150-58

3. H. Ade and A.P. Hitchcock, *Polymer* **2008,** *49,* 643-675.

4. B. O. Leung, A. P. Hitchcock et al. *Macromolecules* **2009**, *42*, 1679 – 1684.

5. B. O. Leung, A. P. Hitchcock et al. *Biomacromolecules* **2009**, in press

6. Research carried out with PEEM2 and STXM532 at the Advanced Light Source, which is supported by Basic Energy Sciences, DoE, USA. Research funded by NSERC.

10:40am **BI-TuM9 Probing Individual Side-Chains of Peptides at Interfaces Using Isotope Labeling with Sum Frequency Generation Spectroscopy**, ***T. Weidner***, *N.F. Breen, G.P. Drobny, D.G. Castner*, University of Washington

Controlled immobilization of peptides onto artificial biointerfaces plays a key role in antifouling, implant and immunosensor technologies and it is of crucial importance to develop tools to examine interfacial properties of adsorbed peptides. Sum frequency generation (SFG) spectroscopy can probe biomolecules at the solid-liquid interface. Isotope labeling can address specific protein regions but its potential in conjunction with SFG spectroscopy has remained mostly unexplored. We combine these techniques to characterize the structure of synthetic model peptides on surfaces in PBS buffer. The peptide used is a 14-mer of hydrophilic lysine (K) and hydrophobic leucine (L) residues with an α-helical secondary structure. These LK14 peptides have the hydrophobic side-chains on one side of the helix and the hydrophilic on the other. Deuteration of the isopropyl group of each of the leucines, totaling 8 samples, was used to probe individual leucine side chains of LK14 adsorbed onto a hydrophobic polystyrene surface. Side-chain orientations were determined using ratios of the asymmetric CD_3 stretching mode at 2221 cm^{-1} acquired with different polarization combinations. We found that the orientation of the leucine side chains in the surface-bound LK14 was remarkably different from the calculated solution structure. Leucines in the center of the peptide are more oriented towards the surface while those at the ends of the amino-acid sequence are more bent away, indicating the leucines in the center of the peptide chain play a dominant role for the binding of the peptide. Solid state NMR data acquired on polystyrene beads is in line with the determined orientation change upon binding. In addition, ^{15}N labeling was used to address the controversial assignment of a pronounced peak near 3300 cm^{-1} observed for a variety of proteins adsorbed onto surfaces. This spectral feature has been assigned to both N-H containing side chains and backbone-related amide A resonances before. ^{15}N labeling of the lysine side chains resulted in a 9 cm^{-1} red-shift of this peak in the spectrum of LK adsorbed onto a SiO_2 surface, showing the 3300 cm^{-1} feature is related to the terminal amine group on the lysine side chains.

11:00am **BI-TuM10 Surface-initiated Vapor Deposition Polymerization of Poly(gamma-benzyl L glutamate): Optimization and Mechanistic Study**, ***W. Zheng***, *C.W. Frank*, Stanford University

Surface-initiated vapor deposition polymerization (SI-VDP) is a highly effective approach to synthesize grafted polypeptides. In this study, we developed an SI-VDP system having pressure and temperature control to reduce vacuum restriction 1000 times with high grafting efficiency and, thus, were able to synthesize grafted poly(gamma-benzyl L-glutamate)(PBLG) film of 167nm thick under 0.75 mbar. More importantly, we quantitatively investigated mechanistic details of the SI-VDP process including monomer vaporization and reservoir polymerization in the monomer reservoir and monomer condensation and physisorbed and chemisorbed polymerization on the substrate surface. To study the major monomer reservoir processes, we monitored the amount of vaporized monomers and developed a VDP reaction profile (VDPRP) method. We found that the VDPRPs were mostly contributed by the reservoir processes. We also found that characteristic features of the VDPRPs were determined by the monomer heating temperature and proposed possible mechanisms for the feature evolution. To evaluate the major substrate surface processes, we developed a quantitative analysis method using FTIR on both as-deposited PBLGs and chemisorbed PBLGs. Consequently, we were able to propose possible SI-VDP mechanisms leading to the surface-grafted PBLGs that were expected to have either high packing density with mostly α-helix segments or low packing density with a significant amount of both random coil and α-helix segments.

11:20am **BI-TuM11 Adsorbed α-Helical Polypeptides: Molecular Organization, Structural Properties, and Interactions**, ***B. Atmaja***, Stanford University, *J.N. Cha,* University of California, San Diego*, C.W. Frank*, Stanford University

In this work, we have developed 11-mercaptoundecanoic acid (MUA)-polypeptide “bilayer” systems by adsorbing poly(diethylene glycol-L-lysine)-poly(L-lysine) (PEGLL-PLL) diblock copolypeptide molecules of various architectures onto MUA-functionalized gold substrates. Previously, we reported the self-assembly of PEGLL-PLL with nanoparticles that were functionalized with carboxylic acid (COOH) moieties to form a variety of supramolecular structures. In relation to this previous work, we have used the PEGLL-PLL/MUA bilayer as a model system for studying the interfacial phenomena that occur when the PEGLL-PLL molecules interact with the COOH moieties of nanoparticle ligands. Specifically, we have elucidated the nature of the interactions between the PEGLL-PLL and COOH moieties as well as the resulting polypeptide conformation and organization, using a combination of surface techniques—grazing-incidence infrared (IR) spectroscopy, ellipsometry, and contact angle. Because our PEGLL-PLL/MUA bilayer system can potentially be applied as a nonfouling surface, we have thoroughly characterized other film properties such as the packing and graft density of the polypeptide molecules as a function of the PEGLL-PLL architecture. A complete understanding of the film's molecular structure would then allow us to elucidate the relationship between the bilayer's nonfouling characteristics and its underlying structure in our future work. Using IR spectroscopy, the adsorption process is determined to occur primarily by means of electrostatic interaction between the protonated PLL residues (pKa ~ 10.6) and carboxylate moieties of the MUA SAM (pKa ~ 6) that is enhanced by H-bonding. The PLL block is thought to adopt a random-coil (extended) conformation, while the PEGLL block that is not interacting with the MUA molecules is found to adopt an α-helical conformation with an average tilt-angle of ~ 60°. The PEGLL-PLL molecules have also been deduced to form a heterogeneous film and adopt a liquid-like/disordered packing on the surface. The average contact angle of the polypeptide/MUA bilayer systems is ~ 40°, which implies that the diethylene glycol (EG2) side chains of the PEGLL residues may be oriented somewhat toward the surface normal. From ellipsometry measurements, it is found that PEGLL-PLL molecules with a longer α-helical block are associated with a lower graft density on the MUA surface compared to those with a shorter α-helical block. This observation may be attributed to the greater repulsion—steric and H-bonding effects—that is imposed by the EG2 side chains found on and projected area occupied by the longer PEGLL block.

Electronic Materials and Processing
Room: A8 - Session EM1+PV-TuM

High Efficiency and Quantum Structure Photovoltaics
Moderator: C.S. Ferekides, University of South Florida

8:00am **EM1+PV-TuM1 Enhancement of the Thermoelectric Figure of Merit in Bulk Semiconductors at the Atomic Level**, ***J.P. Heremans***, The Ohio State University **INVITED**

Recently, several thermoelectric semiconductor systems have been developed with double the thermoelectric figure of merit, zT, of conventional materials. Almost all the progress comes from achieving reductions in thermal conductivity using nanotechnologies or structural disorder. Because the lattice thermal conductivity has a lower limit, the amorphous limit, further progress must come from an enhancement of the electrical properties, in particular the thermoelectric power or Seebeck coefficient. We present a new technique to achieve that, based on creating distortions of the density-of-states by doping with resonant impurities, resulting in a doubling of the zT of PbTe, a semiconductor used for power generation applications near 500 ^{o}C. We will also review current progress with this technique in Bi_2Te_3, the other classical thermoelectric, which we study because the commercial materials used for Peltier cooling are $(Bi_{1-x}Sb_x)_2(Te_{1-y}Se_y)_3$ alloys. The theory behind this approach will be outlined, and its applicability to a wide variety of thermoelectric semiconductors discussed.

8:40am **EM1+PV-TuM3 Synthesis of PbTe Nanowires by Lithographically Patterned Nanowire Electrodeposition (LPNE) and Their Thermoelectric Properties**, ***Y. Yang***, *D.K. Taggart, R.M. Penner, S.C. Kung, F. Yang, C.X. Xiang, M.A. Brown, J.C. Hemminger*, University of California, Irvine

Thermoelectric materials have received renewed interest in the past decade stemming from theoretical calculations that one-dimensional thermoelectric materials (i.e., nanowires) should show a remarkable enhancement in the dimensionless figure of merit—ZT caused by enhanced Seebeck coefficients, electrical conductivities and/or depressed thermal conductivities relative to their bulk counterparts. The prediction has been verified recently on silicon single-crystalline nanowire-arrays that showed almost one hundred times of enhancement of ZT. In contrast, there has not been anydemonstration of a similar effect on PbTe nanowires—one of the best thermoelectric materials in bulk. This presentation reports a synthesismethod called lithographically patterned nanowire electrodeposition (LPNE) for making PbTe nanowires and characterization of their thermoelectricproperties. The nanowires are semi-rectangular in cross-section with width and height independently controlled from 60 to 500 nm and from 10 to 100nm respectively, and they are electrically continuous up to millimeters. The structure and chemical composition of the nanowires are characterizedwith X-ray diffraction (XRD), transmission electron microscopy (TEM) and X-ray photoelectron spectroscopy (XPS). The electrical conductivity and Seebeck coefficient are measured at variable temperatures. A method for making suspended nanowires cross an air gap is also developed, which iscrucial for measurement of thermal conductivity. Ag-doped PbTe nanowires synthesized by the same method demonstrate tunable thermoelectric

properties due to the modification of the carrier type and concentration.

9:00am **EM1+PV-TuM4 PbSe Quantum-Dot Solar Cells**, *K.S. Leschkies, T.J. Beatty, M.S. Kang, D.J. Norris,* ***E.S. Aydil***, University of Minnesota

Quantum confinement of electrons and holes in nanometer size crystals (quantum dots or QDs), endows them with properties that may be advantageous for efficient solar-to-electric energy conversion. First, electronic energy levels and optical absorption in QDs can be manipulated by changing their size. This allows the optimization of their optical absorption for maximum overlap with the solar spectrum. Second, the ability to manipulate energy levels through size raises the possibility to make inexpensive multijunction solar cells by judiciously layering different size QDs. Third, it has been suggested that quantum confinement may slow energy dissipative electron and hole relaxation rates such that two new physical processes, multiple exciton generation and hot electron extraction may now compete with relaxation and lead to higher photocurrents or higher photovoltages, respectively. Finally, QDs can be prepared in large quantities as stable colloidal solutions under mild conditions and deposited on surfaces of various planar or nanostructured substrates as thin films through inexpensive high-throughput coating processes to form photovoltaic devices. For these reasons, solar cells based on QDs may have the potential to achieve high power conversion efficiencies at low cost and are promising candidates for third generation photovoltaic devices. We report a new type of solar cell based on heterojunctions between PbSe QDs and thin ZnO films. We find that the photovoltage depends on the QD size and increases linearly with the QD effective band gap energy. Thus, our solar cells resemble traditional photovoltaic devices based on a semiconductor-semiconductor heterojunction but with the important difference that changing the size of the QDs can vary the band gap of one of the semiconductors and hence the cell's photovoltage. Under simulated 100 mW/cm2 AM1.5 illumination, these QD solar cells exhibit short-circuit currents as high as 15 mA/cm2 and open-circuit voltages up to 0.45 V. Overall power conversion efficiency of the best device to date is 1.6% but may be increased further using nanostructured interfaces between PbSe QDs and ZnO. Moreover, we show evidence that this new solar cell may be operating like an excitonic solar cell rather than a traditional p-n junction solar cell.

9:20am **EM1+PV-TuM5 Phosphonate Self-Assembled Monolayers as Organic Linkers in Quantum Dot Sensitized Solar Cells**, ***P. Ardalan***, *T.P. Brennan, S.F. Bent*, Stanford University

Narrow band gap nanostructures such as cadmium sulfide quantum dots (QDs) are known to show size quantization effects as well as multiple exciton generation. They are therefore beneficial for absorption of light in the visible and near infrared region of the solar spectrum and can be used to fabricate photovoltaic devices with high theoretical efficiencies. In quantum dot sensitized solar cells (QDSSCs), these QDs can be engineered to transfer the electron to a wide band gap semiconductor such as titanium dioxide (TiO_2). However, performance in such devices is reduced by charge recombination at the TiO_2 surface and hence use of organic linkers and electron conductors such as self-assembled monolayers (SAMs) on these devices could provide a means of eliminating recombination sites and lead to increased efficiency. In this study, we investigated the effects of different aliphatic and aromatic SAMs with phosphonic acid headgroups and varied tailgroups on the bonding and performance of cadmium sulfide (CdS) QDSSCs. Our studies focus on bonding of the CdS QDs on both planar and nanoporous TiO_2 with or without the SAM linkers. To study the SAM/QD growth on planar surfaces, TiO_2 was deposited on Piranha-cleaned Si or microscope glass via atomic layer deposition (ALD) and the resulting surfaces were characterized by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), scanning electron microscopy (SEM), and atomic force microscopy (AFM). Next, different SAMs were attached to the TiO_2 substrates from solution, where the effects of chain length, aromaticity, tailgroup, solvent, and dip time on the quality of the SAMs were investigated by the same techniques as well as infrared (IR) spectroscopy, water contact angle (WCA) measurements, and ellipsometry. Finally, CdS QDs were grown on the SAM-passivated TiO_2 surfaces by the successive ionic layer adsorption and reaction (SILAR) process, and the bonding and performance of the resulting materials were evaluated by UV-visible and other spectroscopic techniques. The results were compared to the case of QDs grown on the non-passivated TiO_2 surfaces. Our results show promising differences in the bonding of the CdS QDs at the TiO_2 surfaces with the SAM linkers. We will also present results on the dependence of solar cell performance on the properties of the SAM.

10:40am **EM1+PV-TuM9 High Efficiency Multijunction Solar Cells – Present Status and Future Directions**, ***P. Sharps***, Emcore Corporation **INVITED**

Multi-junction solar cells based on the $GaInP_2$/GaAs/Ge triple junction architecture have achieved the highest efficiency of any photovoltaic device, for either space or terrestrial applications. However, the cost of these cells is high compared to other photovoltaic devices. For space applications (i.e., satellite power) the higher efficiencies are more critical than cell cost, and on a system level, including launch and deployment costs, the multi-junction cells are actually lower on a $/watt basis than Si solar cells. The high efficiency multi-junction cell is now widely used on satellites. For terrestrial applications, the high efficiency cells must be used in high concentration systems where the high cell cost is offset by the lower costs of lenses, mirrors, and structure metal. The cell becomes such a small part of the system cost that a doubling of cell cost has a small effect on the cost of power generation. However, the efficiency of the cell may have a much larger effect on the cost of power generated. So for either space or terrestrial applications the efficiency of the photovoltaic device is very important.

Multi-junction solar cells offer a performance advantage over single junction solar cells because of the reduction in carrier thermallization losses. Different parts of the solar spectrum are absorbed by different band gap materials. III-V materials are able to achieve very high performance on a single junction basis, and when appropriately combined provide an even higher performance advantage. Fortunately, $GaInP_2$, GaAs, and Ge junctions can be combined in a lattice matched configuration, making a monolithic device with a good combination of junctions for converting the solar spectrum into power. Appropriate modifications can be made to the device to optimize it for either space or terrestrial applications.

To achieve even higher efficiencies, more junctions need to be added and/or the junctions need to be better matched to the solar spectrum. A number of approaches have been studied, including novel materials (e.g., InGaAsN, $ZnGeAs_2$, etc.), mechanically stacked devices, and metamorphic devices. With metamorphic devices junctions are grown lattice mismatched on one another to achieve the optimal set of band gaps in a complete device. One metamorphic approach, the inverted metamorphic multi-junction (IMM) solar cell, has demonstrated significant performance improvements over the lattice matched triple junction device.

We report on these improvements, describing how the IMM approach is enabling for both space and terrestrial power generation.

11:20am **EM1+PV-TuM11 GaAs Integration on High-Quality Ge on Si for Multijunction Solar Cells**, ***D. Leonhardt***, *J. Sheng,* 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 cost of multijunction solar cells, we have scaled up a process to produce low-defect-density Ge films on 2-inch-diameter Si substrates. These engineered substrates could replace Ge wafers that are currently used in multijunction solar cell fabrication if the Ge film quality on engineered substrates can match that of commercially available epi-ready Ge wafers. We will present results for the scaled up process of engineered Ge on Si substrates, including key aspects of nucleation, defect formation, and defect reduction/elimination, using a variety of characterization techniques. For ensuing GaAs growth, we polish the Ge surface, using a slurry-free H_2O_2 based chemical-mechanical planarization (CMP) process. This CMP technique results in a root mean square (RMS) roughness less than 1 nanometer as revealed by atomic force microscopy. However, stacking faults in the Ge film that terminate at the film surface show up as raised lines after polishing. We have found that thermal annealing at a very early stage of Ge film growth largely eliminates these stacking faults and produces much smoother films than those grown without the annealing step. We have used a combination of atomic force microscopy and transmission electron microscopy (TEM) to investigate the effect of annealing on eliminating the stacking faults and on the initial Ge island morphology. In addition to defect reduction, we have developed a process for cleaning and passivating the Ge surface in preparation for GaAs growth. GaAs films grown on our engineered substrates have an RMS value of 3.6 nm and show integrated photoluminescence intensity that matches GaAs grown on commercially available off-cut Ge substrates. Future work and directions will be discussed in light of our findings.

11:40am **EM1+PV-TuM12 Investigation of Rare Earth - Doped Silicon Nitride Layers for Solar Cell Applications**, ***M.C. Petcu***, *A. Sarkar, M. Creatore, H.T. Hintzen, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Nowadays the application of thin SiN_x layers as bulk passivating and antireflection coatings for Si-based solar cells applications is considered to be a successful solution for the increase in efficiency[1]. A new concept to further increase the efficiency of the solar cell is based on the light conversion mechanism: according to this approach the solar spectrum can be efficiently modified by shifting the photons towards a wavelength range where the solar cell has a better or higher response[2].

Recently, a novel class of rare earth (RE)- doped SiN_x layers has been demonstrated to be a highly promising red-emitting conversion phosphor for white-LED applications. These materials have allowed the shifting of the emission wavelength by tuning the concentration of a specific RE element in a SiN_x based crystalline matrix[3]. The investigation of RE-doped amorphous silicon nitride (SiN_x) compounds, where the electronic properties of Si are combined with the optical properties of RE^{3+} ions, have been shown already potential in optoelectronics[4]. Therefore, parallel studies on the incorporation of a RE material in amorphous SiN_x host lattices, which could be implemented in solar cells to increase the efficiency, are considered to be presently a challenge.

In this contribution the properties of europium- and samarium- doped amorphous SiN_x layers are investigated. The RE-doped SiN_x layers are deposited using a remote PECVD expanding thermal plasma fed with $Ar/SiH_4/NH_3$ mixtures in combination with a RE magnetron sputtering source implemented in the proximity of the substrate holder. Growth rates of the RE doped layers obtained from Spectroscopic Ellipsometry (SE) measurements were in the range 0.6-2.2 nm/s. The successful incorporation of RE in the SiNx matrix has been demonstrated by means of Rutherford Back Scattering (RBS) and X-ray Photoelectron Spectroscopy (XPS) analysis, i.e. up to 2%. Preliminary photoluminescence results point out a broad band emission in the region of 500-800 nm when excitation wavelengths of 270 nm and 320 nm have been used. The emission band observed can be attributed to Sm^{2+}.

[1] J. Hong et *al*., J. Vac. Sci. Technol. B. 21 (5).

[2] C. Strümpel et *al*., Sol. Energ. Mat. Sol. C. 91 (2007) 238 – 249.

[3] Y. Q. Li et al., J. Alloys. and Comp. 417, 273 – 279.

[4] A. R. Zanatta, et *al*., J. Phys.:Condens. Matter 19 (2007) 436230.

Electronic Materials and Processing
Room: B1 - Session EM2-TuM

Complex and Multifunctional Oxides
Moderator: J.D. Phillips, The University of Michigan

8:00am **EM2-TuM1 Electrical Properties of HfO_2 Thin Films Made by RF Sputtering**, ***B. Aguirre***, *R.S. Vemuri, D. Zubia,* University of Texas at El Paso, *W. Jiang, M.H. Engelhard, V. Shutthanandan,* Pacific Northwest National Laboratory, *C.V. Ramana*, University of Texas at El Paso

Hafnium oxide (HfO_2), which exhibits a very high dielectric constant (*k*) and large bandgap, is considered as a next-generation high-*k* material for application in complementary metal-oxide-semiconductor (CMOS) technology. However, growth of high-quality HfO_2 layers on Si without the formation of interfacial compounds poses a significant challenging problem. The objective of the present work was to optimize the conditions to grow high-quality HfO_2 nanolayered films on Si(100). In our work, HfO_2 films were grown by RF sputtering of HfO_2 ceramic target at various substrate temperatures (T_s= 30-500 ^oC) and studied their structure and electrical properties. $Al/HfO_2/Si$ capacitive structures were fabricated to obtain a metal-oxide-semiconductor (MOS) configuration to mimic the gate stack of CMOS technology and study the electrical properties. Grazing incidence x-ray diffraction (GIXRD) and X-ray photoelectron spectroscopy (XPS) measurements indicate that the effect of T_s is significant on the microstructure. HfO_2 films grown at T_s<200 ^oC are amorphous. An amorphous-to-crystalline transition occurs at T_s=200 ^oC. Nanocrystalline HfO_2 films crystallized in a monoclinic structure with a particle size ~20 nm. XPS measurements indicate the high chemical quality of HfO_2 films grown at T_s=30-500 ^oC. The capacitance-voltage characteristics of the $Al/HfO_2/Si$ devices indicate that HfO_2 films grown (or post-deposition annealed) at 400 ^oC exhibit the expected monoclinic-HfO_2 characteristics.

HfO_2 films exhibit a direct correlation with the microstructure. The results obtained are presented and discussed in detail.

8:20am **EM2-TuM2 XPS Characterization of Hf-based High-k Oxide/SiO_2/Si Films Stacks**, ***E. Bersch***, *M. Di,* University at Albany, *S. Consiglio, R. Clark, G. Leusink,* TEL Technology Center, America, LLC, *A.C Diebold*, University at Albany

As the MOSFET SiO_2-based gate dielectric layer approaches its fundamental physical limits, the investigation of high-k oxides is ongoing in order to determine which oxides can best continue the scaling of the MOSFET. HfO_2, hafnium silicates and nitrided hafnium silicates are leading candidates due to their relatively large band gaps, thermal stability in proximity to Si and relatively high dielectric constants.

The band offsets between the high-k oxide layers and Si in high-k/SiO_2/Si films stacks are important parameters in that the gate leakage current depends strongly on them. Recent studies by various groups have also shown that the threshold voltage in MOSFETs with high-k gate oxides can be altered by the presence of an additional oxide layer such as La_2O_3 or Al_2O_3.[1-3] In the case of a La_2O_3 interface layer, the flatband voltage shift has been correlated with a shift in the energy level alignment in the high-k gate stack.[4]

We have used a combination of x-ray photoemission spectroscopy (XPS) and spectroscopic ellipsometry (SE) to measure the valence and conduction band offsets (VBO and CBO, respectively) between high-k layers and Si substrates. We will report VBO and CBO values for HfO_2, hafnium silicate and nitrided hafnium silicate films with Si. In addition, we will report measurements of the HfO_2-Si band offsets from HfO_2/La_2O_3/SiO_2/Si film stacks, noting the effect of the La_2O_3 layer.

Analysis of XPS spectra of the Si 2p spectra from HfO_2/SiO_2/Si film stacks will also be reported, which shows that the composition of the SiO_2 layer and the energy level alignment between the SiO_2 and Si layers were affected by the growth of the HfO_2 layer and the annealing of the film stack. These results will be discussed with respect to the band offset measurements for HfO_2 film stacks.

Finally, using angle resolved XPS (ARXPS) data we constructed non-destructive compositional depth profiles using a maximum entropy algorithm. A comparison between thickness values extracted from these depth profiles and thicknesses measured with SE will be presented.

References:

1. P. D. Kirsch *et al*., *Appl. Phys. Lett*., **92**, 092901 (2008).

2. V. Narayanan *et al., Symp. VLSI Tech.,* 178 (2006)

3 K. Iwamoto *et al., Appl. Phys. Lett.,* **92,** 132907 (2008)

4. K. Kakushima *et al*., *Appl. Surf. Sci*., **254**, 6106 (2008).

8:40am **EM2-TuM3 Enhanced Dielectric Polarizability of Ge Doped HfO_2 Films on Si and Ge**, ***L. Miotti***, *K.P. Bastos, G. Lucovsky,* North Carolina State University, *D. Nordlund*, Stanford Synchrotron Research Lightsource

The use high dielectric constant materials (high-κ) as gate dielectric in complementary metal-oxide-semiconductor devices based on Si and other higher carrier mobility semiconductors has been focus of intense research. So far, hafnium oxide is among the high-κ dielectrics with higher dielectric constant and higher technologic interest. The most common phase of HfO_2 thin films after deposition and processing is monoclinic with a dielectric constant of κ~ 16-20. However, its dielectric constant can be improved by increasing it in its tetragonal (κ~ 30-35) or cubic phase (κ~ 20-25), which are its thermodynamic equilibrium phases at higher temperatures

We report here on the investigation of Ge doping HfO_2 films and its role in stabilizing the tetragonal phase of hafnium oxide phase. The films were deposited by remote plasma enhanced chemical vapor deposition on both Si(001) and Ge(001) substrates. Hf-t-butoxide and GeH_4 were used as source for Hf and Ge, while O_2 as the oxidizing agent. Germanium concentration in the films was determined by Auger electron spectroscopy. Interface reaction was hindered by nitridation of the substrates before the deposition of the films. Conventional x-ray diffraction analysis is not suited to investigate the crystallographic order in very thin films (< 10 nm), as well as those of interest for device applications. Therefore, we probed the local symmetries by x-ray absorption spectroscopy using the beam line 10 in SSRL.

The x-ray absorption spectra for 2 and 5 nm thick HfO_2 films deposited on Si with 0, 5, or 15 at.% Ge, as well as the second derivative of these spectra was studied. Based on previous studies of HfO_2 films on Si, the shape of the transitions to the E_g and T_{2g} states of the 5 nm thick film without Ge doping corresponds to a monoclinic phase with a different Jahn-Teller distortion than the trigonal. A significant change in these features is observed when the film is doped with 5 at.% Ge. In this case the E_g and T_{2g} transitions correspond to a tetragonal symmetry. Higher germanium doping leads to a mixture of monoclinic and tetragonal phases causing a broadening of the absorption spectra. There is not significant difference in the absorption spectra for the 2 nm thick films with different doping, indicating that the Ge stabilization of a tetragonal phase can only be achieved above a critical thickness.

The mechanism that stabilizes the tetragonal phase of HfO_2 using a tetravalent dopant is significantly different from that associated with trivalent impurities as yttrium, which involves oxygen vacancies. This mechanism results in decrease of the c/a ratio with no vacancies involved.

9:00am **EM2-TuM4 Correlated Oxide Heterostructures**, ***R. Ramesh***, The University of California, Berkeley **INVITED**

Complex perovskite oxides exhibit a rich spectrum of functional responses, including magnetism, ferroelectricity, highly correlated electron behavior, superconductivity, etc. The basic materials physics of such materials provide the ideal playground for interdisciplinary scientific exploration. Over the past decade we have been exploring the science of such materials (for example, colossal magnetoresistance, ferroelectricity, etc) in thin film form by creating epitaxial heterostructures and nanostructures. Among the large number of materials systems, there exists a small set of materials which exhibit multiple order parameters; these are known as multiferroics. Using our work in the field of ferroelectric and ferromagnetic oxides as the background, we are now exploring such materials, as epitaxial thin films as well as nanostructures. Specifically, we are studying the role of thin film growth, heteroepitaxy and processing on the basic properties as well as magnitude of the coupling between the order parameters. In this talk I will describe to you some aspects of such materials as well as the scientific and technological excitement in this field.

9:40am **EM2-TuM6 Polarization-dependent Electron Tunneling Into Ferroelectric Surfaces**, ***P. Maksymovych***, *S. Jesse,* Oak Ridge National Laboratory, *P. Yu, R. Ramesh,* University of California, Berkeley, *A.P. Baddorf, S.V. Kalinin*, Oak Ridge National Laboratory

Electron tunneling underlies numerous devices relevant to information technology and has been proposed in future energy harvesting and quantum computing applications. Replacing a conventional insulator in the tunnel junction with an electronically correlated material can yield new types of electronic functionality. In one such concept, dubbed ferroelectric tunneling, the tunneling barrier height is controlled by the polarization of a ferroelectric oxide, enabling non-volatile conduction states that can be switched with electric field. Although ferroelectric tunneling has been thoroughly theorized, a convincing experimental demonstration of this phenomenon is still lacking. The key challenge is to find a material system that simultaneously satisfies the dimensional constraints for tunneling and ferroelectricity, as well as to assure that the conductance is not dominated by extrinsic effects of charge injection and filamentary conduction, which is ubiquitous in complex oxides.

In this talk we will demonstrate a highly reproducible polarization control of local electron transport through epitaxial $Pb(Zr_{0.2}Ti_{0.8})O_3$ films. Despite being 30-50 nm thick, conductive atomic force microscopy revealed that the films possessed spatially and temporally reproducible local conductivity in the regime of Fowler-Nordheim electron tunneling. This is likely due to a strong electric field in the sub-surface region (excess of 10^6 V/cm) created by the relatively sharp metal tip. Local I-V characteristics exhibited strong hysteretic behavior across the surface. By combining conducting atomic force microscopy with piezoresponse force microscopy, we have, for the first time, directly correlated local events of ferroelectric and resistive switching [1]. The large spontaneous polarization of PZT produced as strong as 500-fold enhancement of FN-tunneling conductance upon ferroelectric switching, sufficient to demonstrate a local non-volatile memory function. The physical mechanism of the observed effect was traced to the polarization-dependence of the height and possibly width of the metal-ferroelectric Schottky barrier.

By observing the role of inherent disorder in ferroelectrics and comparing films grown on different electrode materials, we have shown that the switching voltage and the magnitude of conductance hysteresis are subject to electrostatic control via ferroelectric switching. Variable-temperature measurements and local effects due to dielectric non-linearities will also be discussed.

[1] P. Maksymovych, S. Jesse, P. Yu, R. Ramesh, A. P. Baddorf, S. V. Kalinin, Science (2009) *in press*.

10:40am **EM2-TuM9 XAS and XPES Studies of Strongly Correlated Ti d-states in $Gd(Sc_{1-x}Ti_x)O_3$**, ***G. Lucovsky,*** North Carolina State University, *C. Adamo,* Penn State University, *D.L. Schlom,* Cornell University, *K.B. Chung*, North Carolina State University

There is considerable interest in complex oxides comprised of transition metal, TM, and lanthanide rare earth, LRE, atoms with room temperature magnetic properties that can modulated by electrical input. Ferro- and ferrimagnetic properties require strongly correlated spin sub-bands derived from TM(LRE) d(f)-states, and have been reported in elemental oxides: CrO_2 and Fe_3O_4, and EuO_2. Strongly correlated bands are created by a double exchange mechanism requiring a transition to a metallic state. The incorporation of tetravalent Ti into a d^0 complex oxide with trivalent Gd and Sc, requires that Ti be in a formal trivalent valence state, Ti^{3+}. Alloying with Ti then introduces a d^1 occupied state into the complex oxide host in direct proportion to the Ti content.

$Gd(Sc_{1-x}Ti_x)O_3$ alloys > 5 nm thick with x = 0.0, 0.01, 0.05, 0.18 and 0.25 were deposited at room temperature in an UHV system onto (i) $LaAlO_3$ substrates for epitaxial growth, and (ii) superficially oxidized Si(001) to produce nano-grain films. As-deposited nano-grain dimensions are 2-2.5 nm, and are too small for Jahn-Teller distortions and spin ordering of Ti alloy atoms. The correlation exchange energy for spin correlated bands is obtained from room temperature films on Si is approximately equal to the energy difference between the localized Ti impurity state energy and Sc band edge d-state.

A compositionally dependent insulator/metal transition is reported for the first time in $Gd(Sc_{1-x}Ti_x)O_3$ alloys for x > 0.16, and is attributed with a correlated Ti d-state band. This insulator to metal transition is identified by X-ray absorption spectroscopy, XAS, extending into the pre-edge regime for X-ray energies <530 eV. Annealing at 900°C in Ar increases grain size enabling Jahn-Teller distortions, and results in an insulator to metal transition evidenced by opening of a gap between oppositely directed Ti spin states. This insulator to metal transition is also observed in as-deposited epitaxial films as well, and consistent with percolation theory, only if the Ti concentration exceeds a critical concentration of ~16.5 %, as in the 18 and 25 % alloys. Differentiation of XAS spectra indicates ferrimagnetism, with a second partially occupied spin band. As predicted by theory, the separation of these spin bands is the same as the correlation exchange energy obtained from the Ti impurity band energy.

This transition is also observed in X-ray photoemission spectroscopy, XPES. The dominant correlated spin band is below the $Gd(Sc_{1-x}Ti_x)O_3$ alloy Fermi level energy in the XPES spectra, and the oppositely directed spin band is at the Fermi level energy.

11:00am **EM2-TuM10 ZnO/$LiNbO_3$ Heterojunctions: A Candidate System For Multifunctional Oxides**, ***E. Cagin***, *J.D. Phillips*, University of Michigan, Ann Arbor

Ferroelectric/semiconductor heterostructures are desirable for multifunctional devices using the charge of a ferroelectric material to manipulate the conductivity of a semiconductor. The quality of the ferroelectric/semiconductor interface is critical for maintaining a significant ferroelectric polarization charge density, and coupling this charge density into the semiconductor. Therefore, materials must have excellent chemical and structural compatibility. ZnO and $LiNbO_3$ may provide the desired characteristics based on the crystalline compatibility of the materials, excellent semiconducting properties of ZnO, and excellent ferroelectric properties of $LiNbO_3$. In this work, the structural and electrical characteristics of ZnO thin films deposited on z-cut $LiNbO_3$ substrates by pulsed laser deposition will be presented and compared to ZnO thin films on c-plane sapphire substrates. In all experiments, preferentially-oriented c-plane ZnO thin films were obtained based on x-ray diffraction measurements.

Hall effect measurements demonstrate a background carrier concentration in ZnO of n=2. $6x10^{17}cm^{-3}$ for ZnO/$LiNbO_3$, and an order of magnitude decrease of $n=3.0x10^{18}cm^{-3}$ for ZnO/sapphire. Similarly, an improved electron mobility of $\mu=36\ cm^2/Vs$ is observed for ZnO/$LiNbO_3$ in comparison to $\mu=21\ cm^2/Vs$ for ZnO/sapphire. The reduced carrier concentration and improved mobility are attributed to a depletion layer at the ZnO/$LiNbO_3$ interface induced by polarization charge. The temperature dependence of electron transport in ZnO thin films will also be presented to examine the influence of polarization charge induced by the pyroelectric effect in $LiNbO_3$.

11:20am **EM2-TuM11 The Study of Electrical and Structural Properties of SiO_2 Film Containing Metal oxide using Organosiloxane-based Silica Precursor**, ***K. Watanuki***, *A. Inokuchi*, Tohoku University, Japan, *A. Banba, H. Suzuki, T. Koike, T. Adachi*, Ube-Nittou Kasei Co., Ltd., Japan, *A. Teramoto, Y. Shirai, S. Sugawa, T. Ohmi*, Tohoku University, Japan

High quality SiO_2 film formation is important for many applications as electrical insulator films, protective films for semiconductor, alkali-dissolution barrier films and antireflection films on the glass. In some of applications, the electrical property of the films plays an important role. Various techniques have been used thus far in preparing SiO_2 films. Especially, in various techniques, sol-gel technique has significant advantage compared with other techniques with uniformity of thickness, damage free, easy coating of large surfaces, homogeneous multi-component oxide films, controllability of compositions, and potential industrial application. So, in this work, we have evaluated the electrical and structural characteristics of SiO_2 film using organosiloxane-based silica precursor. And we have evaluated the influence of additives to organosiloxane-based silica precursor, such as TiO_2, HfO_2, Ta_2O_5, ZrO_2 and several kinds of metal oxide components on the electrical and structural property of these SiO_2 base insulator films.

The organosiloxane-based sol-gel material investigated here is derived from the mixture of tetraethoxysilane (TEOS) and methyltrimethoxysilane (MTMS) by changing the molar ratio of TEOS/MTMS. In the case of the addition of metal oxide to SiO_2 matrix, such as TiO_2, HfO_2, Ta_2O_5, ZrO_2 and several kinds of metal oxide, metal alkoxides such as tetraisopropoxytitanate (TPOT) were added in the concentration ranging from 1 to 15 mol %. In order to evaluate the electrical property of films, we fabricated MOS (Metal-Oxide-Silicon) devices.

By controlling mixing molar ratio between TEOS and MTMS in the sol-gel precursor, the dielectric constant of films can be controlled. This sol-gel precursor was prepared not only of perfect silica film but also a dense film through optimized conditions such as the pre-baking for 5 min at 130˚C, N_2 ambience low pressure gas removing process continuously increasing the temperature up to 900˚C, and oxidation process using O_2/H_2O at 900˚C. In this study, the influence of additives to the sol-gel precursor was examined on the structural and electrical property of the SiO_2 based films derived from the sol-gel precursor. The breakdown voltages of the resultant films were effectively improved by adding a small amount of metal oxide such as TiO_2, HfO_2, Ta_2O_5 and ZrO_2. It was found that the SiO_2 based film derived from the sol-gel precursor added with metal oxide components, such as TiO_2, HfO_2, Ta_2O_5 and ZrO_2, had excellent uniformly-structured Si-O-Metal bond and that the electrical insulation property of the film was improved by the concentration of metal oxide additives.

Exhibitor Workshops
Room: Exhibit Hall 1 - Session EW-TuM

Exhibitor Workshop
Moderator: B.R. Rogers, Vanderbilt University

10:20am **EW-TuM8 A New Ion-Trap based Vacuum Quality Monitoring & Measurement System**, ***K. Van Antwerp***, *G.A. Brucker, J. Rathbone, S. Blouch, M. Schott*, Brooks Automation, Inc.

Granville-Phillips, a Brooks Automation Product Line, is introducing the Series 850 VQM vacuum quality monitoring and measurement system for 1-300amu mass range applications that is comprised of a high speed Total and Partial Pressure Ionization Gauge Sensor and High Performance Vacuum Gauge Controller. Vacuum Quality Measurement (VQM) requires the ability to measure both total and partial pressures and is linked to yield, throughput and uptime improvements in vacuum applications. The ideal VQM system must offer real-time information, should be easy-to-use and calibrate, must offer uninterrupted operation, and seamless data analysis and information delivery. The Series 850 VQM provides these features with 100amu range VQM measurements in 100ms for new visibility into the gas-specific components of a vacuum system pressure burst, high-speed leak and gas-specific monitoring and detection, no zero-blast accurate hydrogen and helium measurements, and VQM driven real-time analog, digital and setpoint relay outputs. The Series 850 VQM gauge can be easily mounted to the vacuum system by remote cable connection to the Vacuum Gauge Controller and calibrated using an automated single gas calibration system. The Series 850 VQM has a graphics display for total and partial pressure measurements, gas specific trend display, and front panel operation. The Series 850 VQM supports instrument automation through Ethernet and USB interfaces and a full set of software tools.

Graphene Topical Conference
Room: C3 - Session GR+EM+MS-TuM

Graphene and Carbon-based Electronics
Moderator: J.E. Rowe, North Carolina State University

8:00am **GR+EM+MS-TuM1 Graphene: Quantum Transport in a 2D Membrane**, ***C.N. Lau***, University of California, Riverside **INVITED**

Graphene, a two - dimensional single atomic layer of carbon, has recently emerged as a promising candidate for electronic materials, as well as a new model system for condensed matter physics. It also has the double identity of an extraordinary conductor and the thinnest isolated membrane. In this talk I will present our results on both of these aspects: (1) our observation of novel transport phenomena in graphene, including coherent interference of multply-reflected charge waves and properties of p-n-p junctions in zero and high magnetic fields; and (2) our work on ripple formation and manipulation on suspneded graphene sheets. I will conclude the talk with a brief discussion on the fascinating prospect of strain-based graphene engineering.

8:40am **GR+EM+MS-TuM3 Air Induced Suppression of n-Type Conduction in Field-Effect Transistors**, ***P. Levesque,*** Université de Montréal, Canada, *C.M. Aguirre,* École Polytechnique de Montréal, Canada, *M. Paillet, F. Lapointe,* Université de Montréal, Canada, *B.C. St-Antoine, P. Desjardins,* École Polytechnique de Montréal, Canada, *R. Martel*, Université de Montréal, Canada

Carbon nanotube, graphene, and organic semiconductor based devices share common features when exposed to atmospheric environment. For carbon nanotube field-effect transistors (FET), the effect is an almost exclusive p-type character in air. N-type conduction can only be observed under certain conditions, for instance when the devices are annealed in vacuum. By performing experiment under controlled atmosphere, we investigated the impact of the chemical nature of the substrate and of gas adsorbates on the field-effect switching behavior of both nanoscale and thin-film nanotube FETs. Our study revealed that the intrinsic material properties are modified and lead to the reduction of n-type conduction when an adsorbed water layer containing solvated oxygen is present on the SiO$_2$ surface. This finding demonstrates that an electrochemical charge transfer reaction between the semiconducting channel and the aqueous oxygen redox couple is the underlying phenomenon behind the suppression of electron conduction in nanotube devices. The impact of this redox couple on graphene FET explored in this context will also be discussed. We forecast that these redox active species generally influence the transport properties of transistors operating in air and propose a general mechanism that explains behaviors observed in many material systems on SiO$_2$/Si substrates, also including nanowires, polymers and organic materials.

9:00am **GR+EM+MS-TuM4 Epitaxial Graphene Device Technology**, ***D.K. Gaskill,*** U.S. Naval Research Laboratory, *J. Moon,* HRL Laboratories, LLC, *J.L. Tedesco,* U.S. Naval Research Laboratory, *J.A. Robinson,* The Pennsylvania State University, *A.L. Friedman, P.M. Campbell, G.G. Jernigan, J.K. Hite, R.L. Myers-Ward, C.R. Eddy, Jr.,* U.S. Naval Research Laboratory, *M.A. Fanton*, The Pennsylvania State University

Recently, the world's first graphene RF field effect transistors (FETs) have been fabricated using photolithography on epitaxial graphene (EG) grown on 50 mm SiC semi-insulating wafers. The RF FETs had f_{max} of 14 GHz at 5 V_{ds} for 2 µm gate widths and results are expected to improve as gate widths are scaled down. Continued research addressing key materials issues is needed to push the performance metrics for devices fabricated on wafer-scale EG significantly higher. Some of these key materials issues are morphology and thickness control, enhanced mobility, uniformity of sheet carrier density and resistivity, and optimizing atomic layer deposition (ALD) of high dielectric constant oxides on EG. In this presentation, we will present details on our approach using Si sublimation from SiC substrates for growing EG on 50.8 and 76.2 mm diameter SiC wafers and discuss the impact of key material issues on RF device performance.

.

Epitaxial graphene was synthesized using a commercial Aixtron VP508 SiC epitaxial growth reactor on the Si- and C-faces of 4H- and 6H-SiC semi-insulating 0° oriented substrates at temperatures from approximately 1225 to 1700°C and for times ranging from 10 to 300 min. Substrates were 16 x 16 mm^2 coupons and 50.8 and 76.2 mm diameter wafers. Both *in-vacuo* (10^{-6} to 10^{-4} mbar) and Ar ambient (50-200 mbar) Si sublimation synthesis conditions were investigated. Dielectrics were deposited using a Cambridge NanoTech Savannah 200 ALD system. EG was characterized by a wide array of tools including atomic force, Nomarksi and scanning tunneling microscopies, Raman spectroscopy, Hall effect, and Lehighton contactless resistivity and mobility wafer probe.

.

The growth of EG on 50.8 mm Si-face wafers using the *in-vacuo* process was optimized and excellent relative resistivity uniformity of 2.8% and record 300 K Hall mobilities up to 2700 $cm^2V^{-1}s^{-1}$ were found. Raman spectroscopy mapping of the 2D peak on the wafers determined: (1) the majority of the film was monolayer EG, (2) two layers of EG could be found at step edges and (3) the EG was continuous across the wafer. RF FETs fabricated using the latest optimized wafer-scale EG exhibited state-of-the-art ambipolar behavior, I_{on}/I_{off} ratios and peak transconductances. Frequency performance metrics were established for these devices such as $f_T \bullet L_g$ products of 10 GHz●µm and f_{max} of 14 GHz. To our knowledge, the highest field effect mobilities reported to-date have been measured using these devices. We will discuss the impact of key material parameters associated with EG for these record results as well as the impact of Ar ambient controlled graphenization on future RF devices.

9:20am **GR+EM+MS-TuM5 Hydrogen Adsorption at Surfaces of the Epitaxial Graphene on the 6H-SiC(0001)**, *Y. Aoki,* ***H. Hirayama***, Tokyo Institute of Technology, Japan

Recently, adsorption of a small amount of atomic hydrogen was reported to transform the exfoliated graphene from highly conductive semimetal into an insulator [1]. In this case, the C-atom is only the site for hydrogen adsorption. However, at the epitaxial graphene on the SiC(0001) substrate, hydrogen could adsorb on both C- and Si-site. Furthermore, the surface structure changes by stages from Si-rich 3x3, $\sqrt{3}$x$\sqrt{3}$ to C-rich 6$\sqrt{3}$x6$\sqrt{3}$ phase in the epitaxial growth of graphene on SiC substrates [2]. In this study, we investigated the hydrogen adsorption at these surfaces appeared in the way of epitaxial growth of graphene on the Si-terminated 6H-SiC(0001) surfaces.

Experiments were carried out in an ultra-high vacuum apparatus equipped with a Si dozer, a LEED/AES, a TPD (Temperature Programmed Desorption), a hydrogen gas inlet, and a hot W-filament. We prepared the 3x3, $\sqrt{3}$x$\sqrt{3}$, and 6$\sqrt{3}$x6$\sqrt{3}$ surfaces by heating the sample at 850°C under the Si flux, heating at 1150°C for 3min, and heating at 1250°C for 3min, respectively. We exposed these surfaces to atomic hydrogen, and measured their TPD spectra. Our TPD indicated that the saturation coverage of H was ≈0.1 monolayer (ML) at these surfaces independent of the surface structure. However, the TPD spectrum changed drastically at the stage from 3x3 to $\sqrt{3}$x$\sqrt{3}$. The 3x3 surface showed a shoulder at ≈500K, and a dominant peak at 700K, while the $\sqrt{3}$x$\sqrt{3}$ and the 6$\sqrt{3}$x6$\sqrt{3}$ surface had a single peak at 400K. Comparing to the previous TPD studies at graphite [3], we attributed to the single peak at 400K to the hydrogen desorption from the graphene layer. Meanwhile, the peak at 700K of the 3x3 surface is very close to the hydrogen desorption peak from the Si(111) surface. Both TPD and AES suggests that the π-bonded C-induced benzene ring structure started to grow at the appearance of the $\sqrt{3}$x$\sqrt{3}$ surface structure. This interpretation is supported by our electron energy loss spectroscopy (EELS) measurements in which the π-plasmon loss peak of the benzene ring started to evolve at the $\sqrt{3}$x$\sqrt{3}$ surface.

[1] Science 323,610(2009), [2]JPC,B208,19912(2004), [3]JCP117,8486(2002)

9:40am **GR+EM+MS-TuM6 Graphitic Carbon Growth on Si(111) from Solid Source Molecular Beam Epitaxy**, ***J.C. Hackley,*** *D. Ali, J. Di Pasquale, C.J.K. Richardson*, University of Maryland, College Park

Since the recent discovery of isolated graphene through mechanical exfoliation of bulk graphite, a number of methods have been developed to produce graphene. However, there have been no reports of graphene growth by direct carbon deposition such as solid source molecular beam epitaxy (MBE). Carbonization of a silicon surface is a commonly used first step in the epitaxial growth of SiC films, and is often accomplished by solid source MBE of carbon onto a Si substrate to form a thin SiC buffer layer. Annealing SiC wafers in ultra-high vacuum is a reliable method of producing graphene layers, and is frequently referred to as an epitaxial technique. Consequently, graphene may be synthesized via MBE through a two-step process consisting of first growing SiC, and then annealing this film at high temperatures to desorb Si. A shorter processing route which bypasses the SiC formation would be quite beneficial. In this project, we investigate the growth of graphene directly on Si using solid source MBE at growth temperatures which are much lower than a SiC process.

An EPI-Model 930 MBE system which has been modified to accommodate a Si electron beam source is used for carbon sublimation onto 3" Si wafers. Our carbon source is a Thermionics rod-fed electron beam gun with a highly oriented pyrolytic graphite (HOPG) target. Reflective high-energy electron diffraction (RHEED) measurements are used to monitor the carbon film growth in situ. The film bonding structure is investigated ex-situ with x-ray photoelectron spectroscopy (XPS), Fourier transform infrared spectroscopy (FTIR), and Raman scattering spectroscopy. Film topology is examined ex-situ with scanning electron microscopy (SEM) and atomic force microscopy (AFM). Hall measurements in a Van der Pauw configuration are implemented for electrical characterization of the films. Through preparing the Si surface with seeding layers and choosing an appropriate C flux we have been able to suppress SiC formation and grow graphitic carbon at temperatures < 700°C. Raman scattering measurements show the G mode at ~1600 cm^{-1} and the D mode at ~1320 cm^{-1} (Fig. 1), as well as weak overtones of these phonon modes. XPS analysis of the C 1s region shows no significant sp3 carbon bonds, and no SiC formation, which is also verified by FTIR measurements (Fig. 2). SEM and AFM analysis show that the films are smooth and continuous.

We are currently refining our growth process in order to increase graphite grain size and subsequently downscale to 2-dimensional growth. These initial results appear promising for the future development of graphene growth via direct deposition of carbon.

10:40am **GR+EM+MS-TuM9 Epitaxial Graphene: Designing a New Electronic Material**, ***W.A. de Heer***, Georgia Institute of Technology **INVITED**

Since 2001 the Georgia Tech epitaxial graphene research team and its collaborators have developed the new field of epitaxial graphene electronics.The current status of epitaxial graphene research will be presented, including the production methods and recent results from various characterization investigations. Methods have been developed to grow continuous multilayerd epitaxial graphene (MEG) on the C-face of hexagonal silicon carbide with of up to 100 graphene sheets and its extraordinary transport properties have been demonstrated.

Surprisingly, the properties of MEG are closely related to monolayer graphene rather than graphite, as a result of an unusual rotational stacking of the graphene layers that causes the graphene sheets to electronically decouple. Consequently the electronic band structure of MEG is composed of Dirac cones. The charge carries are chiral and exhibit a non-trivial Berry 's phase. Weak anti-localization and quantum confinement has been demonstrated. Landau level spectroscopy further exhibits record-breaking room temperature mobilities and well resolved Landau levels below 1 T, indicating extremely low carrier densities and good homogeneity of the material. Efforts towards large scale electronic device patterning will be reviewed.

11:20am **GR+EM+MS-TuM11 MORTON S. TRAUM AWARD FINALIST: Room Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene**, ***Q.H. Wang*****, *M.C. Hersam*, Northwestern University

Graphene has attracted significant attention due to its unique electronic structure, high carrier mobilities, and quantum relativistic phenomena. Epitaxial graphene grown on SiC(0001) is a promising material for next-generation technology because it allows for wafer-scale processing. In order to realize its full potential for a diverse range of devices, the bare graphene sheet must be incorporated with other materials via chemical functionalization schemes. Recent progress reported in the literature include the demonstration of atomic layer deposition of Al_2O_3 on mechanically exfoliated graphene sheets functionalized by carboxylate-terminated perylene derivatives,[1] and the formation of monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) at cryogenic temperatures on epitaxial graphene.[2] In this study, we report the room-temperature formation of self-assembled monolayers of PTCDA on epitaxial graphene.[3] We characterize the molecular ordering and electronic properties of these monolayers using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The molecules self-assemble into stable, well-ordered monolayers that are arranged in a herringbone phase with extended domains spanning hundreds of nanometers. At submonolayer coverage, PTCDA forms stable, isolated molecular islands. The molecular ordering is unperturbed by either defects in the epitaxial graphene or atomic steps in the underlying SiC surface. Scanning tunneling spectroscopy (STS) performed on the PTCDA monolayers reveals strong features in the electronic density of states that are distinct from the pristine graphene regions. The demonstration of robust, uniform organic functionalization of epitaxial graphene presents opportunities for exploring self-assembly chemistry on graphene, tailoring the chemical functionality of graphene, and templated growth and deposition of other materials as potential routes toward realizing graphene-based molecular electronic and sensing devices.

[1] X.R. Wang, S.M. Tabakman, and H.J. Dai, *J. Am. Chem. Soc.* **130**, 8152-8153 (2008).

[2] P. Lauffer, K.V. Emtsev, R. Graupner, T. Seyller, and L. Ley, *Phys. Status Solidi B*, **245**, 2064-2067 (2008).

[3] Q.H. Wang and M.C. Hersam, *Nature Chemistry*, in press (2009).

11:40am **GR+EM+MS-TuM12 Effects of Reducing Conditions on Conductivity Change of Graphene Oxide**, ***H. Asano***, *Y. Shimogaki*, The University of Tokyo, Japan

Graphene is an attractive material for electronic devices since it has remarkable electronic properties, such as super high electron mobility. There are some methods to form graphene on SiO_2, however, it is difficult to cover SiO_2 substrate fully by flat graphene flakes on a wide area. For example, micromechanical cleavage of graphite can make graphene sheet on SiO_2, but the largest size of it will be within several micrometers. There is a demand, however, to graphene to use as conductive materials such as wiring material for ULSI interconnects and transparent and conductive electrode for solar cells and flat panel displays. These applications require large area coating and low process temperature. Then, graphene oxide (GO) coating and its reduction to form conductive graphene gets much attention. In the present work, we tried to reduce GO by gas-phase reduction and examined the resistivity change.

To obtain GO dispersion, graphite (Nippon Graphite Industry Co., LTD, SCB-100) was oxidised through the modified Hummer's methods. The dispersion was determined to be 0.965 wt% from the weight change of the dispersion. The dispersion was exfoliated by sonication, diluted by ethanol to 0.20 wt% and spin-coated on SiO_2/n-Si substrate, which was pre-treated by aminopropyltriethoxysilane (APTES). Spin-coated GO film was dried at room temperature. Reduction of GO film to form graphene was carried out in a vacuum, H_2, or formic acid ambient. The temperature of the substrate was ranged from 200°C to 1000°C, base pressure was 2.6×10^{-7} Torr, pressure of reducing agent (hydrogen or formic acid) was 5 Torr.

Thickness of spin-coated GO film was 30±5 nm and the film contents were 90 at% of C and 10 at% of O. Sheet resistance of the film was decreased by annealing in vacuum. The reciprocal of sheet resistance showed the Arrhenius type behaviour and minimum sheet resistance obtained in our work was 0.7 kΩ/sq. This result suggests some thermal activation phenomena that controls resistivity of GO. Thermal Desorption Spectroscopy (TDS) analysis showed that almost all O atoms were removed at 200°C, but very small amount of H_2O, CO, CO_2 was also detected above 200°C. The elimination of remaining oxygen as H_2O, CO, CO_2 at high temperature may be responsible for the Arrhenius type behaviour of the sheet resistance. Sheet resistance became one-third by the reduction using formic acid at 290°C compared with the reduction in vacuum or H_2. The sheet resistance treated over 700°C did not show any ambient dependency. We will also discuss the chemical bond state change observed by XPS and carrier concentration / mobility change measured by Hall measurement.

Nanometer-scale Science and Technology
Room: L - Session NS+TR-TuM

Modeling Nanoscale Phenomena
Moderator: S.B. Sinnott, University of Florida

8:20am **NS+TR-TuM2 Tribological Behavior of Nanostructured Materials Predicted from Molecular Dynamics Simulations**, ***E. Bucholz***, *T. Liang, S.R. Phillpot, S.B. Sinnott*, University of Florida

Nanostructured materials such as fullerenes and nanotubes have been of much interest to tribologists since the discovery of C_{60}, buckminsterfullerene, in 1985. Characterized by weak van der Waals (vdW) forces that govern the interactions between these nanostructured materials, low friction coefficients are obtained through combinations of rolling, sliding, and rotating at the sliding interface. This presentation will report on the tribological properties of onion-like carbon (OLC) fullerenes with and without a residual diamond core as a solid lubricant between two sliding, diamond-like carbon (DLC) surfaces. The molecular dynamics (MD) simulations presented here utilize the reactive empirical bond order (REBO) potential for short range interaction coupled with the Lennard-Jones (LJ) potential for long range vdW interactions Within these simulations no discernable difference is predicted between the OLC fullerenes with a diamond core and those without. Further, the frictional behavior of these systems is highly dependent on the interactions that take place between the fullerenes and the DLC substrates. Without the formation of bonds with the substrates, the OLC fullerenes in the simulations are able to roll providing extremely low frictional forces, but as bonds begin to form, the OLC fullerenes begin to slide which causes a significant increase in the observed friction. The presentation will also report on the mechanical properties of molybdenum disulfide (MoS_2) nanotubes and their response when used as solid lubricants between two sliding Mo surfaces. Variations in number of nanotube layers, temperature, and compressive load are examined in order to characterize each system. The authors acknowledge the support of the National Science Foundation Grant No. CMMI-0742580.

8:40am **NS+TR-TuM3 High Pressure at Small Scales in Tribology and Piezoelectronics: Insights from First-Principle Molecular Dynamics**, ***M.H. Müser***, University of Western Ontario, Canada **INVITED**

At very small scales, many solids have the ability to sustain extremely large pressures before wearing off, i.e., up to a few GPa. Some materials, deposited on top of such hard solids, undergo chemical changes at these pressures, thereby changing their mechanical or electrical properties dramatically. In my talk, I will discuss how first-principle molecular dynamics can be used to analyze the mechanisms responsible for changes in the response functions of the deposited materials. Specific examples will be zinc phosphates (ZPs), in their function as anti-wear additives in commercial lubricants, and doped pnictogen solids (DPSs), when used in

---

* Morton S. Traum Award Finalist

non-volatile electronic memory or in programmable switches. Molecular dynamics reveals when and why ZPs show "smart material" properties and anticipate the possibility for DPSs to be switched with nanoscale piezoelectronic actuators.

9:20am **NS+TR-TuM5 Optical Energy Density Inside Metallic Nano-Apertures**, ***P. Zhu***, *H. Craighead*, Cornell University

We use numerical methods and calculate the optical energy density inside a sub-micron sized hole surrounded by metallic cladding as light wave travels through it. Such information is important in the use of Zero-Mode-Waveguides (ZMWs) [1], where the diameter of the apertures is less than the wavelength of the light. In ZMWs, it has been postulated the evanescent wave inside the aperture defines the illumination volume, which is a function of the illumination wavelength and the aperture cut-off wavelength, which is in-turn a function of the aperture-diameter. Although the cut-off wavelength of a circular hole in an infinitely thin perfect conductor is a monotonically increasing function of the hole diameter [2], we see from our calculation result that, inside apertures surrounded by aluminum cladding, optical energy density increases until it reaches a peak as aperture diameter increases, and then levels off as aperture becomes more transmitting. This result suggests that, in order to achieve the best signal-to-noise ratio in fluorescent single-molecule experiments involving ZMWs, there is an optimal aperture diameter for each wavelength and application.

[1] Levene et al, “Zero-Mode Waveguides for Single-Molecule Analysis at High Concentrations, Science, Vol 299, 2003.

[2] Jackson, J. D., Classical Electrodynamics, 1998.

9:40am **NS+TR-TuM6 Field Amplification in Surface-Enhanced Raman Scattering**, *E.J. Adles*, ***S. Franzen***, *D.E. Aspnes*, North Carolina State University

Surface-enhanced Raman scattering (SERS) is experiencing renewed popularity as a result of the present interest in nanostructures and reported observations of SERS from single molecules. However, the detailed reasons for enhancements, which have been reported to be as much as 10^{14}, remain unclear. We address the issue from a fundamental perspective that has provided insight into the physics of second-harmonic generation and other nonlinear-optical processes, considering metallic spherical inclusions for simplicity. One obvious result, although it contradicts many statements in the literature, is that resonant-plasmonic enhancement of both incident and emitted waves by the same sphere is impossible, since the sphere cannot simultaneously exhibit plasmonic resonances at the frequencies w_o and w_R of the driving and Raman fields, respectively. The presence of an adjacent inclusion nominally resonant at the other frequency does not resolve the issue due to coupling by the longitudinal (Coulomb) interaction. However, under certain circumstances amplification can occur at a second frequency by means of a resonance activated by a renormalization of the effective mass of the bonding electrons of the molecule due to their longitudinal interactions with the sphere. Local configurations in deposited thin films where this could occur would likely be extremely rare, but cannot be ruled out completely.

Plasma Science and Technology
Room: A1 - Session PS1-TuM

Advanced FEOL and BEOL Etch
Moderator: Y. Kimura, LAM Research

8:00am **PS1-TuM1 Inductively-Coupled Pulsed Plasmas in the Presence of Synchronous Pulsed Substrate Bias for Advanced Gate Etching**, ***S. Banna***, Applied Materials Inc., *K. Tokashiki*, Samsung Elect. Co. Ltd., *A. Agarwal*, Applied Materials Inc., *J.Y. Lee*, Samsung Elect. Co. Ltd., *V. Todorow*, Applied Materials Inc., *J.H. Yoon*, Samsung Elect. Co. Ltd., *S. Rauf*, Applied Materials Inc., *K. Shin*, Samsung Elect. Co. Ltd., *K. Ramaswamy, P.J. Stout, D. Lymberopoulos, K. Collins*, Applied Materials Inc. **INVITED**

The pace at which microelectronics technology is progressing is highly challenging with conventional device architecture. The stringent and conflicting requirements in microelectronics for damage-free plasma etching processes, with improved uniformity, higher selectivity, better anisotropy, more precise ion energies/fluxes control and enhanced process throughput have stimulated an intensive research effort among academic and industrial communities. This research is focused on novel approaches for the design/control of the next generation of plasma processing reactors. Following the above challenges, the dry etch process regime for gate etching has moved towards low pressure plasmas with higher densities. In this regime, the risk of plasma induced damage(PID) or charging damage increases, potentially affecting the overall device electrical performance. PID includes UV damage and highly energetic ion bombardment damage. Moreover, for high aspect ratio structures, electron shading effect becomes more dominant enhancing the risk of charging damage. In the past, it was demonstrated that pulsed radio frequency(PRF) inductively coupled plasmas(ICP) have the promise to address some of the above challenges. Typical commercial ICP reactors consists of 2 RF power supplies, the RF source which is fed to the antenna coils of the ICP source and RF bias applied to the substrate. Accordingly, 3 main different regimes of operation for pulsed plasmas might take place. The first, known as source pulsing, in which the source is operating in PRF mode while having the bias in continuous wave(CW) mode. The second is bias pulsing i.e. source in CW mode while the bias is in PRF mode. The third one is synchronized pulsing, for which both source and bias are pulsed simultaneously at the same frequency and duty cycle.

Recently we have evaluated the impact of synchronized pulsing plasma on gate etch for sub-50nm DRAM applications. The evaluation included basic etching characteristics such as average etch rate, uniformity and selectivity, 35nm gate critical dimension(CD) uniformity and profile control, and plasma induced damage. It was demonstrated that by control of the synchronous pulse parameters extends the plasma operating conditions range aiming to improve processes for finer features. In particular, we have shown gate CD controllability, PID mitigation, and significant reduction in electron shading effect and in the gate leakage current along with improving the electrical performance of the overall device. 2D plasma and feature scale modeling results will be used to illustrate the basic physics of synchronous pulsing, in particular its effect on the ion energy distribution.

8:40am **PS1-TuM3 Synchronously Pulsed Capacitively Coupled Plasma Sources for Dielectric Etching**, ***A. Agarwal***, *P.J. Stout, S. Rauf, K. Collins*, Applied Materials Inc.

Plasma etching processes for microelectronics fabrication at future technological nodes are extremely challenging. The requirements regarding the uniformity (both etch rate and critical dimensions) are also more stringent than ever. One particular challenge in plasma etching of extremely high aspect ratio features (aspect ratio > 40) is minimizing plasma induced damage, both physical and electrical. The via-like features may physically twist/turn due to the stochastic nature of fluxes entering the feature as the size of the opening shrinks.[1] Charge trapped by the polymer on the sidewalls exaggerates this phenomenon. Alternately, charge retention at the bottom of trenches may lead to breakdown as the material stresses under the accumulated charge creating a weak path for the injected current.[2] Pulsed plasma operation has been shown to be a promising approach to improving uniformity while reducing charge damage.[3] Although pulsing of both capacitively and inductively coupled plasma sources has been investigated before, novel pulsing schemes such as synchronous pulsing in multi-frequency capacitively coupled plasmas (CCP) may allow for expanded operating regime for damage-free etching of high aspect ratio features.

In this paper, pulsed and continuous plasma operation of a multiple frequency capacitive coupled plasma reactor in electronegative gas mixtures will be discussed using results from a computational investigation. A 2/3-dimensional plasma equipment model (CRTRS) [4] has been linked to a Monte Carlo feature profile model [5] to assess the consequences of pulsed plasma operation on etching of dielectric features. Results will be discussed for impact of pulse characteristics such as duty cycle, pulse excitation frequency, phase lag between source and bias pulses on dielectric etching in a multi-frequency CCP chamber. Careful tailoring of pulsing at both source and bias frequencies enables negative charge acceleration in the features and helps negate charge buildup. The impact of varying plasma electronegativity at different gas pressures will also be discussed. If strongly electronegative gas mixtures are used, sustaining a steady pulsed plasma can however be complicated as the plasma may not re-ignite after power is turned-off.

[1] A. Agarwal, M.M. Wang, and M.J. Kushner, 54th AVS Symposium 2007.

[2] T. Ohmori and T. Makabe, Appl. Surf. Sci. 254, 3696 (2008).

[3] S. Banna, et al., 55th AVS Symposium 2008.

[4] A. Agarwal, P.J. Stout, S. Rauf and K. Collins, 61st Gaseous Electronics Conference 2008.

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

9:00am **PS1-TuM4 Highly Selective and Low Damage Etching of TiN / HfO_2 Layer Gate Stack Structure using Neutral Beam Etching and Atomic Layer Etching**, ***B.J. Park***, *J.B. Park, TH. Min, J.K. Yeon, S.K. Kang, W.S. Lim, G.Y. Yeom*, SungKyunKwan University, South Korea, *K.S. Min*, University of Texas, Austin

As the critical dimension of metal-oxide-semiconductor field-effect transistor shrinks less than 45 nm and below, conventional polysilicon gates on ultrathin SiO2 dielectric layers should be replaced by metal gates on high-k dielectric materials. However, the adoption of these new materials imposes new integration problems. Among many integration issues, the etch selectivity of the etched layers (metal electrode or high-k dielectrics) to the under-layers (high-k dielectrics or Si substrate) is one of the most important issues in the patterning of the gate stack structures.

In order to solve these problems, in this study, we applied two step etch process where, the metal gate electrode is selectively etched using a reactive neutral beam against a high-k dielectric layer and then the high-k dielectric layer is removed using atomic layer etching (ALET) for precise etch depth control.

The result showed nearly infinite etch selectivity of TiN/HfO2 using a HBr/Cl2 neutral beam by controlling energy (<100 eV). In addition, an anistropic etch profile and smooth surface roughness (0.109 nm) could be observed using TEM and AFM. For the ALET of HfO2, the monolayer etching condition of 1.2 Å /cycle could be observed using BCl3 ALET and, after the 30 etch cycles, exactly 3.5nm thick HfO2 layer was removed with a low surface roughness and without the change of surface composition. When we compared the properties of MOSFET devices fabricated using conventional RIE processing and those using the neutral beam/atomic layer etching, the improvement of characteristics of NMOSFET and PMOSFET could be observed for the devices fabricated using neutral beam /atomic layer etching.

ACKNOWLEDGMENT

This work supported by the National Program for Tera-Level Nano devices of the Korea Ministry of Education, Science and Technology (MEST) as a 21st Century Frontier Program.

9:20am **PS1-TuM5 Impact of Cure and Trim Processes on the Linewidth Roughness Transfer during Gate Stack Patterning with Amorphous Carbon Mask**, ***L. Azarnouche***, STMicroelectronics, France, *E. Pargon, M. Martin, O. Luere, K. Menguelti*, CNRS/LTM, France, *P. Gouraud, C. Verove,* STMicroelectronics, France, *O. Joubert*, CNRS/LTM, France

With the continuous scaling down of semiconductor device dimensions, the linewidth roughness (LWR) becomes a non negligible parameter that needs to be controlled in the nanometer range for the future technological nodes (1.7nm (3σ) for the 32 nm technological node). In previous studies, we demonstrated that the 193 nm photoresist mask LWR is the main contributor to the final gate LWR. We also observe that the LWR is mainly decreased during the plasma etching steps in which the resist mask is involved (BARC and hard mask etching). Preliminary conclusion is that the photoresist mask is the first vector of LWR decrease during plasma exposure. The resist LWR is therefore the key parameter to sucessfully control the final metal gate LWR in the nanometer range. In the present study, we first evaluate the impact of HBr cure plasma treatment and resist trimming processes on the resist LWR and second analyze how these plasma etching steps impact the final gate LWR. LWR measurements are performed using the CD-AFM technique much more powerful than commonly used CD-SEM. First results indicate that both resist trimming and plasma cure treatment processes improve the resist LWR and consequently the final gate LWR. We demonstrate that, during cure processes, plasma Vacuum UltraViolet (VUV) light is mainly responsible for the resist LWR decrease while during trim processes, the plasma VUV light combined to the lateral erosion of the resist induced by reactive radicals is identified as the main contributor to the resist LWR decrease.

However, we also show that the sequence of cure and trim processes has a less important impact on the gate LWR than a cure or a trim process only and that the position of the cure treatment in the sequence of plasma etching steps involved in the gate patterning process has some consequences in the final gate LWR. Finally, as the etching mask used to pattern the gate plays a primordial role in the final gate LWR, we compare the impact of two masking strategies: one using amorphous carbon layer as etching mask and the other one a spin on carbon hard mask.

9:40am **PS1-TuM6 Multilayer Mask Etch - CD, CD Bias, and Profile Control using RLSA Plasma Etcher**, ***H. Kintaka***, *T. Mori,* TEL Technology Center, America, LLC USA, *M. Sasaki, 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), CD bias, and the mask profile control technique has been needed. As the result of this study, precise CD control of multilayer mask etching was established by RLSA (Radial Line Slot Antenna) microwave plasma source. The multilayer stack which was used for experiments consisted of Photo Resist/SiARC/Organic/SiN/Si-substrate.

The results are: first, zero Iso/Nest bias was accomplished. As result, the same CD bias is obtained kept in both the Iso and Nest pattern with vertical profile. Second, CD Bias is controlled in the range of several +/- nm with same bias of Iso/Nest by adjusting SiARC etching condition. By these characteristics, it is possible to make hard mask CD same as patterned resist CD in any pattern density.

These results are obtained by RLSA micro-wave plasma characteristics. RLSA generates high density plasma just below top dielectric plate, and as the plasma diffuses forward the wafer, its density and electron temperature become lower by diffusion. The etched by-products do not re-dissociate and not deposit on the wafer in the low electron temperature condition. This result shows that this plasma can etch only biased ion direction without side-wall deposition.

These unique characteristic will remove the burden of adjusting the width in the patterning step.

10:40am **PS1-TuM9 Effects of Hydrogen Bombardment during Polysilicon Gate Etching by HBr/O$_2$ Plasmas**, ***T. Ito***, *K. Karahashi,* Osaka University, Japan, *M. Fukasawa, S. Kobayashi, N. Kuboi, T. Tatsumi,* Sony Corporation, *S. Hamaguchi*, Osaka University, Japan

As the miniaturization of semiconductor devices continues, better control techniques of substrate surface damages as well as a better understanding of the mechanisms of surface modification during plasma processing are required for future semiconductor manufacturing. Especially during etching processes by HBr/O$_2$ plasmas, which are widely used for etching of polysilicon gate electrodes, it has been reported that the silicon substrate under a gate oxide film is seriously damaged during the gate electrode etching process. This phenomenon is known as a “Si recess”. The goal of the present study is to understand the cause of the Si recess and to propose a technique to minimize it. To understand the mechanism, we have used a multi-beam injection system, which can irradiate surfaces with independently controlled atoms, molecules and ions. In this way, the system enables us to simulate experimentally plasma-surface interactions that take place during plasma etching processes. The multi-beam system consists of three parts, i.e., a mass analyzed ion beam injector, a set of two independently controllable neutral radical/molecular beam injectors, and a reaction chamber in which a sample substrate can be placed. In this system, a monochromatic and mono-energetic ion beam as well as independently controlled radical/molecular beams can be simultaneously injected into a given substrate surface. The ion and radical sources are differentially pumped and therefore the chamber can be maintained at ultra-high vacuum. The change in chemical nature of the substrate surface can be observed *in situ* by X-ray photoelectron spectroscopy (XPS) that is installed in the reaction chamber. In this study, Si(100) surfaces were irradiated by H$^+$, Ar$^+$, or O$^+$ ion beam at 500eV each as well as atomic oxygen (O) radical beams and are analyzed with (*ex situ*) High-Resolution Rutherford Backscattering (HRBS). The results have shown that a layer of structure alteration with 10 nm thickness is formed on the Si substrate surface only when H$^+$ ions are injected into the surface. Furthermore it has been found that oxygen (O) diffusion is enhanced in the alteration layer due to amorphization of Si. Thus our multi-beam injection experiments corroborates the hypothesis that the Si recess during HBr/O$_2$ plasma etching processes is caused by H$^+$ ion injections from HBr plasmas and O radical diffusion. This also suggests the importance of precise control of incident ion energies for the minimization of Si recesses during the processes.

11:00am **PS1-TuM10 Challenges in Etching sub-45nm Shallow Trench Isolation (STI)**, ***A. Paterson***, *T. Panagopoulos, S. Sriraman, A. Sato, N. Benjamin, N. Williams, C. Lee, Y. Yamaguchi-Adams, A. Eppler, L. Braly, T. Kim, H. Singh, V. Vahedi*, Lam Research

The continued scaling in semiconductor industry provides new challenges for etching Shallow Trench Isolation (STI) features to create active area islands. Control of the STI profile is of primary importance, e.g. trench angle control of 88° ± 0.2° being requested across a 300 mm wafer, along with the additional demand to control the trench depth range non-uniformity to <2.5%, for ~2500-3000 Å trench depth. Typically, the stringent profile control requirements are met by operating halogen based Transformer Coupled Plasma (TCP^{TM}) plasmas in the mid-pressure operating regime, 20mT to 60mT. However, in this regime the trench depth non-uniformity is upward of 5% and has a characteristic wafer pattern that resembles a “donut”, which is due to the electron mean free path, λ_{mfp}, being short (e.g. 0.85cm for 20mT Cl2) compared to the chamber dimensions. The electrons and ions are predominately produced in the TCP’s torroidal power deposition region, with the torroid pattern then being transferred to the wafer plane through ion diffusion. The trench depth pattern can be substantially reduced by operating at lower pressure <5mT, such that the λ_{mfp} is comparable to the chamber dimensions and energized electrons can ionize neutrals with almost equal efficiency across the chamber, where the shape of the plasma density determined only by ambipolar diffusion. However, this severely inhibits profile control with trench angle and selectivity requirements not being met.

This paper will discuss the work undertaken at Lam Research to characterize halogen plasma's produced by the TCP configuration of a Kiyo^{TM} process chamber. Plasma diagnostic and simulation data shows that the plasma density uniformity can be substantially improved for a given pressure operation regime by optimizing the TCP hardware configuration. This optimization will translated into achieving <2.5% trench depth uniformity at mid pressure operation whilst maintaining profile control. Future challenges facing STI trench depth etch will also be discussed.

11:20am **PS1-TuM11 Control of TiN Sheet Resistance in Downstream Plasma PR Strip**, *V. Vaniapura, **L. Diao**, S. Xu*, Mattson Technology, Inc.

Semiconductor integrated circuit density has increased continuously by shrinking the device size. Interconnects between multiple stacked metal layers need to be moved closer together hence thinner and narrower. However, the reduction of the interconnect dimensions increases electrical resistance and a subsequent loss of device performance. This leads to an ongoing effort to search for materials with lower electrical resistance suitable for interconnects to integrate into IC production. Metals like tungsten, titanium are good choices but require the use of conductive diffusion barriers. Titanium nitride (TiN) is widely employed as diffusion barrier layer and/or adhesion layer due to its low sheet resistance (Rs). Integration challenges occur with TiN during high temperature photoresist (PR) strip. The commonly used PR removal process, down stream oxygen plasma, can increase sheet resistance of TiN significantly. In order to understand how to reduce this adverse effect on the TiN layers, extensive studies of sheet resistance change (ΔRs) were conducted. TiN samples were treated with plasma exposure of different chemistries in an inductively coupled plasma reactor. Optical emission spectroscopy (OES) was used to observe the presence of reactive species in the plasma of different chemistries. The experimental results show that pure reducing chemistries were effective in maintaining the Rs, and the addition of these reducing chemistries to oxygen plasmas can significantly reduce ΔRs. OES analyses indicate that ΔRs is mainly caused by the oxidation of TiN with the present of reactive oxygen species in the plasma. Reactive oxygen content is controlled by the percentage of reducing chemistry in total flow. The dependences of ΔRs of TiN to various process parameters were investigated in detail. A majority of the Rs shift happens in the first tens of seconds of plasma exposure, which indicates that it is caused by modification of top surface. Based on this work, an optimized chemistry and process regime have been identified to greatly reduce or even suppress sheet resistance increase without compromising PR removal productivity.

11:40am **PS1-TuM12 Inductively Coupled Plasma Etching of GaN and Induced Defects**, ***J. Ladroue***, GREMI - STMicroelectronics, France*, A. Meritan, M. Boufnichel,* STMicroelectronics, France*, P. Lefaucheux, P. Ranson, R. Dussart*, GREMI, France

Wide bandgap materials such as gallium nitride are currently used for light emitter devices [1]. Otherwise, GaN physical properties open new prospects in microelectronics manufacturing [2]. By combining a wide bandgap (3.4 eV), strong chemical bonds and high electronics mobility, GaN based devices should operate under higher temperature, higher power and higher frequency than typical silicon devices.

GaN etching is one of the first process steps in device structure developments. Due to inert chemical nature of GaN, wet etching is limited [3]. As a consequence, it is necessary to use dry etching method [4] to obtain a reliable MESA structures. Chlorine plasmas are commonly used because GaCl3 is the most volatile etching product. Due to the strong bond energy of III nitrides, GaN etching also requires high physical sputtering which is provided by heavy neutral gas like argon and high bias voltage.

In this study, the GaN etching was performed into an industrial Alcatel 601 E tool which consists of an Inductively Coupled Plasma source and a diffusion chamber [5]. This high density plasma system was initially dedicated to silicon deep etching and modified to use chlorine gases. Plasma is generated by a single-ring antenna coupled to a RF power supply operating at 13.56 MHz. The 6 inch chuck is independently biased and thermally regulated. The process gases including argon and chlorine (Cl2) are injected at the top of the source.

Cl2/Ar plasma etching was performed on GaN epitaxial layers (12µm) grown on sapphire by metalorganic chemical vapor deposition (MOCVD). After SiO2 deposition by Plasma Enhanced Chemical Vapor Deposition (PECVD), wafers were patterned using conventional photolithography. Samples were subsequently mounted on 6 inch coverplates made of different materials.

We have carried out a parameter screening to optimize the etch efficiency of GaN. The best results in term of profile quality are obtained with a silicon coverplate. An etch rate of 250 nm/min is reached with our current setup. However, defects like columns or pits are observed at the etched surface under some conditions. The origin of those defects is also investigated in this study. Moreover, diagnostics such as Langmuir probe, optical emission spectroscopy and mass spectrometry have been used to characterize the plasma and understand the etching mechanisms.

References:

[1] H. Morkoc, Wide Band Gap Nitrides and Devices, Springer, Berlin, 1998.

[2] G.T. Dang et al., IEEE Trans. Elect. Dev., vol. 47 (2000) 692

[3] D. Zhuang et al., Mater. Sci. & Eng., R 48 (2005) 1–46

[4] S.J. Pearton et al., J. Appl. Phys., Vol. 86 (1999)

[5] M. Boufnichel et al., JVST B, 20 1508 (2002)

Plasma Science and Technology
Room: B2 - Session PS2-TuM

Atmospheric Plasma Processing and Microplasmas
Moderator: Y. Sakiyama, UC Berkeley

8:00am **PS2-TuM1 Microplasma Synthesis of Dimensionally- and Compositionally-Controlled Metal Nanoparticles for Catalytic Growth of Carbon Nanotubes**, *W.-H. Chiang, **R.M. Sankaran***, Case Western Reserve University

Microplasmas operated at atmospheric pressure in a continuous-flow geometry have tremendous potential for gas-phase nanoparticle synthesis. The non-thermal decomposition of vapor precursors in combination with the limited reaction volume afforded by microplasmas allows the fabrication of narrow dispersions of nanometer-sized particles (< 5 nm) *in a single step*. We have recently applied this technique to the synthesis of mono- and bimetallic nanoparticles for catalytic carbon nanotube (CNT) growth [1-3]. Dimensionally- and compositionally-controlled nanoparticles are initially prepared in a microplasma from metal-organic precursors such as ferrocene and nickelocene. To catalyze CNTs, acetylene and hydrogen gases are added to the particle flow exiting the microplasma reactor and heated in a tube furnace. Here, we show that the structure of as-grown CNTs is intimately related to the size and composition of the nanocatalysts. Reducing the mean diameter of the nanocatalysts to ~2 nm results in a high-purity of single-walled CNTs in the reactor product (>75 %). At a constant mean particle diameter, compositional tuning of bimetallic nanocatalysts is found to significantly alter the chirality distributions of the collected single-walled CNTs. In this talk, we will present the synthesis methodology, as well as detailed materials characterization of both the nanocatalysts and the CNTs.

1. W-H. Chiang and R. M. Sankaran, "Microplasma synthesis of metal nanoparticles for gas-phase studies of catalyzed carbon nanotube growth," Appl. Phys. Lett., Vol. 91, 121503 (2007)

2. W-H. Chiang and R. M. Sankaran, "Synergistic effects in bimetallic nanoparticles for low temperature carbon nanotube growth," Adv. Mater., Vol. 20, 4857 (2008).

3. W-H. Chiang and R. M. Sankaran, "In-flight dimensional tuning of metal nanoparticles by microplasma synthesis for selective production of diameter-controlled carbon nanotubes," J. Phys. Chem. C, Vol. 112, 17920 (2008).

8:20am **PS2-TuM2 Argon-Methyldisiloxane-Oxygen Fed Atmospheric Pressure DBDs for SiO_2-like Thin Film Deposition**, ***F. Fanelli**, S. Lovascio, R. d'Agostino, F. Fracassi*, University of Bari, Italy

Organosilicon compounds, such as for instance hexamethyldisiloxane (HMDSO), mixed with oxidants (i.e. O_2 or N_2O) and noble gases (i.e. Ar, He), are widely used both in low pressure and atmospheric pressure plasma enhanced chemical vapour deposition (PE-CVD) of SiO_2-like coatings. In particular very recently atmospheric pressure dielectric barrier discharges (DBDs) fed with organosilicon monomers have been addressed as an attractive route towards the deposition of thin films. Since the deposition mechanism is not definitively known intense research efforts should be directed to the identification of the main reaction steps and to the correlation of the plasma chemistry with the coatings properties. For this reason in this work we report our recent results on the deposition of SiO_x thin films with atmospheric pressure DBDs fed by argon (Ar) in mixture with oxygen (O_2) and different methyldisiloxanes, i.e.

hexamethyldisiloxane, pentamethyldisiloxane and tetramethyldisiloxane. The characterization of the deposited films was carried out by XPS, FTIR and SEM. The quali-quantitative determination of stable by-products contained in the exhaust gas, and formed by plasma activation, was performed by gas chromatography coupled with mass spectrometry (GC-MS). The influence of feed composition, in terms of chemical structure of the organosilicon compound and of the oxygen-to-monomer feed ratio, on the properties of the films as well as on monomer depletion and by-products concentration, was investigated.

Results show that in the absence of O_2 polymer-like coatings are deposited. Oxygen addition to the feed leads to a decrease of the carbon content of the film which is more evident when the number of methyl groups in the monomer is lower. GC-MS analyses allowed to appreciate that many linear and cyclic compounds, containing up to five silicon atoms, are formed in the plasma. As an example, in the case of HMDSO, the presence of species containing the dimethylsiloxane (-Me_2SiO-) repeating unit appears to be indicative of oligomerization processes (e.g. chain propagation, ring formation, and expansion reactions) which bring to linear and cyclic compounds with general formulas Me-$(Me_2SiO)_n$-$SiMe_3$ ($n = 1$-4) and $(Me_2SiO)_n$ ($n = 3$ - 4), respectively. The extent of unreacted monomer does not depend significantly on the feed composition even if the O_2-to-HMDSO feed ratio is varied in a wide range (i.e. 0-25). However, O_2 addition influences the quali-quantitative distribution of by-products.

The results allow to support hypotheses on the nature of films precursors as well as to clarify some aspects of the overall deposition mechanism and of plasma-surface interaction.

8:40am **PS2-TuM3 Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition by Homogeneous Dielectric Barrier Discharge**, ***N. Gherardi***, *L. Maechler, I. Enache, C. Sarra-Bournet, N. Naudé, H. Caquineau,* LAPLACE - CNRS - Université de Toulouse, France, *F. Massines*, Promes - CNRS, France **INVITED**

Low pressure plasma enhanced chemical vapor deposition (LP-PECVD) is widely used in the industry since it allows obtaining thin films without any substantial temperature increase. On the other hand, these last years, there has been an increasing interest in atmospheric pressure PECVD (AP-PECVD) since it can lead to an appreciable cost reduction. The potential cost saving is related to the suppression of the vacuum equipment and to the on-line processing capability.

In case of two dimensional materials such as rolls of thin polymer films, metal foils or glass plates, dielectric barrier discharge (DBD) appears as one of the most suitable discharges because it is a cold discharge, which is robust, and not disturbed by the motion of the substrate. DBDs normally operate in the usual filamentary mode, but it is now well-known that depending on the gas, electrical parameters, and electrode configuration, DBDs can also operate in homogeneous modes. Depending on the gas in which they are ignited, these homogeneous DBDs generally present different features. In the rare gases (helium, argon, neon…) they are known as atmospheric pressure glow discharges (APGD) as they are characterized by high current densities and an electric field profile between the electrodes showing a cathode fall, a negative glow, a Faraday dark space, and a positive column. In nitrogen, they are called atmospheric pressure Townsend discharge (APTD) as they show lower current densities and a constant high field in between the electrodes.

If AP-PECVD can be achieved using filamentary discharges, the filamentary and statistical nature of this regime leads most of the time to a lack of control of the thin film quality, deposition rate and coating uniformity on large surface. Hence this paper focuses on an AP-PECVD process using homogeneous DBDs.

More precisely, we report here on the deposition of silicon based thin films using homogeneous DBDs working at atmospheric pressure, from hexamethyldisiloxane (HMDSO) diluted either in N_2 or in He, with or without small admixture of nitrous oxide (N_2O) as the oxidizing gas. Our approach consists in studying the thin film properties as a function of the discharge type (APGD or APTD) and N_2O content in the gas phase, using various surface analysis techniques: ellipsometry, profilometry, scanning electron microscopy, Fourier-transform infrared spectroscopy and X-ray photoelectron spectroscopy (XPS). The gas phase is characterized mainly through optical emission spectroscopy. Results obtained either without motion of the substrate or in a roll-to-roll configuration are discussed, showing the capability of AP-PECVD to realize multilayers.

9:20am **PS2-TuM5 On the Deposition Mechanism of the Silica Like Films in Atmospheric Pressure Glow Discharge**, ***S.A. Starostin***, Eindhoven Univ. of Technology, The Nethelands, The Netherlands, *A.P. Premkumar,* Materials Innovation Institute (M2i), The Netherlands, *M. Creatore,* Eindhoven Univ. of Technology, The Netherlands, *H. de Vries, R.M.J. Paffen,* FUJIFILM Manufacturing Europe BV, The Netherlands, *M.C.M. van de Sanden*, Eindhoven Univ. of Technology, The Netherlands

Atmospheric pressure plasma enhanced thin film deposition (PECVD) is nowadays in focus of increasing scientific and industrial interest. The benefits of this newly emerging technology are in possibilities for cost-efficient in-line roll-to-roll production without expensive and cumbersome vacuum equipment. Yet, comparing to the well studied low pressure PECVD, there is a serious lack of insights on thin film deposition mechanisms on the moving substrates at high pressure.

In this contribution we present a study of the deposition process of silica-like films in the diffuse high power variety of the dielectric barrier discharge referred as atmospheric pressure glow discharge (APGD) [1, 2]. This process is capable to produce uniform carbon-free silica-like films on the polymeric webs in low cost gas mixtures [2]. Considering deposition mechanisms in a roll-to-roll atmospheric PECVD reactor with a moving polymer substrate and gas flow, three different pathways which are simultaneously contributing to the film formation can be identified: a) ionic deposition, where ionized products of the decomposed precursor drift in the electric field towards the surface; b) diffusive deposition of neutral radicals produced in plasma and afterglow phases and c) deposition of large particles or dust. Due to the gas flow and depletion of the precursor, each of these mechanisms leads to layers characterized by a specific composition, morphology and location within the discharge area. In this contribution we will address the influence of the different mechanisms on film deposition, supported by space-resolved spectroscopic ellipsometry, XPS, SEM and water contact angle measurements. The experimental profiles of the deposition rate along the gas flow were analyzed with a 2D numerical convection-diffusion deposition model.

[1] S. Okazaki, M. Kogoma, M. Uehara, Y. Kimura, J. Phys. D: Appl.Phys., **26**, 889, (1993)

[2] S.A. Starostin, M.A. ElSabbagh, E. Aldea, H. de Vries M. Creatore, M.C.M. van de Sanden, *IEEE Trans. Plasma Sci*. **36**, 968 (2008)

[3] S. Starostine, E. Aldea, H. de Vries, M. Creatore, M. C.M. van de Sanden, Plasma Process Polym, **4**, S440 (2007)

9:40am **PS2-TuM6 Industrial Scale Pulsed Atmospheric Dielectric Barrier Discharges**, ***B.D. Schultz***, *W.M. Hooke, W.F. Hargrove, A.R. Martin*, International Technology Center

Atmospheric dielectric barrier plasma glow-like discharges over 1 meter in length and 500 square centimeters in area have been generated in air with a custom high voltage driving source. Pulse peak currents well in excess of 1 kiloampere at atmospheric pressure with total charge transfer up to 90 microcoulombs have been repeatedly generated in homogeneous discharges at frequencies up to 100 hertz. A rapid voltage rise time at 20-30kV is readily achieved by the source and is sufficient to produce a voltage across the electrodes in excess of the DC breakdown voltage prior to the onset of breakdown. The overvoltage condition plays an important role in determining the uniformity of the plasma discharge. Electrical modeling of the discharge characteristics show the resistivity of the plasma to change over the course of an individual pulse causing the discharge characteristics to switch from an oscillatory state to a critically damped state. Charge transfer and power densities in dielectric barrier discharges are limited by the electrode size and the intrinsic material properties of the dielectric used to distribute the space charge. It will be shown that the charge transfer of each pulse scales proportionally with the size of the electrodes for a given dielectric as should be expected for a complete homogeneous discharge. This paper will emphasize the correlation between overvoltage conditions, dielectric material properties, and electrode size to the electrical charge transfer of the glow-like discharge. The impact of the charge transfer scaling behavior on the scaling of other critical parameters like current density will also be discussed.

10:40am **PS2-TuM9 Optical Emission Spectroscopy of an Argon DC Microdischarge: Electron Density and Gas Temperature Profiles**, ***S.G. Belostotskiy****, *T. Ouk, V.M. Donnelly, D.J. Economou,* University of Houston, *N. Sadeghi*, Université Joseph Fourier de Grenoble, France

Optical Emission Spectroscopy was employed to study a high pressure (100s of Torr) DC microdischarge in argon, with traces of N_2 and H_2 present and acting as optical tracers. Spatially resolved measurements of gas temperature across the 600 μm slot-type discharge were obtained from analysis of the rotational structure of two transitions of the first positive

---

* PSTD Coburn-Winters Student Award Finalist

band of N_2: $B^3\Pi_g(v=4) \rightarrow A^3\Sigma_u^+(v=1)$ and $B^3\Pi_g(v=5) \rightarrow A^3\Sigma_u^+(v=2)$. Gas temperature profiles peaked at the cathode side of the discharge and slowly decreased towards the anode. Such behavior is consistent with the physics of DC discharges, where most of the power dissipation occurs in the cathode layer. The gas temperature increased with increasing current, reaching a maximum of T_g = 1200 K at I = 30 mA and P = 600 Torr. Electron densities were extracted from the spectral profile of the H_β line. The profile was fit with a Voigt function, which included Doppler, pressure, instrumental and Stark broadening. The electron density was estimated from the contribution of Stark broadening. The spatial profile of electron density was found to have a maximum in the cathode sheath edge region, followed by a minimum in the bulk plasma, and then a maximum some distance from the anode. This spatial distribution was explained by the non-homogeneous structure of the microdischarge, having a highly contracted positive column. The electron density near the sheath edge increased with both pressure and current reaching $n_e = 1.7 \cdot 10^{14}$ cm^{-3} at I = 30 mA and P = 600 Torr.

11:00am **PS2-TuM10 Argon Microplasma Diagnostics by Diode Laser Absorption**, ***N. Miura***, *J. Xue*, *J. Hopwood*, Tufts University

Argon gas kinetic temperature and the resonance state ($1s_4$) density in argon microplasma were measured by tunable diode laser absorption[1]. The experimental argon gas pressure was varied from 1 to 760 torr. A 900 MHz microstrip split ring resonator[2,3] was used as the microplasma generator. A single-mode diode laser was tuned to scan through the argon 801.4nm line ($1s_4$-$2p_7$) by modulating the diode's driving current. The output of the diode laser was collimated and passed through the microplasma. The obtained absorption lineshapes were fit by a Voigt profile, which is the convolution of Gaussian and Lorentz profiles. The Gaussian part corresponds to Doppler broadening and the Lorentz part corresponds to collisional and Stark broadening. Under our high-pressure experimental conditions, collisional broadening dominates and Stark broadening are almost negligible. Since the Doppler and collisional broadening can be expressed by a single variable T (gas temperature), the absorption lineshapes were fit with two parameters, amplitude and gas temperature[4]. The line integrated density of the resonance state was estimated from the integral of the absorption profile. The line integrated densities of argon $1s_4$ are $1.7\text{x}10^{15}$ m^{-3} m at 1 torr and $1.4\text{x}10^{15}$ m^{-3} m at 760 torr with 1W of input power. The visually observed length of plasma decreases from 1 cm at 1 torr to a few hundred microns at 760 Torr. The measured gas temperature increases from 350 K at 1 Torr to 750 K at 760 Torr. The microplasma is also simulated using a fluid model, which is compared with experimental measurements.

[1] D. Bear and R. Hanson, J. Quant. Spectrosc. Radiat. Transfer **47**, 455 (1992).

[2] F. Iza and J. Hopwood, Plasma Sources Sci. Technol. **14**, 397 (2005).

[3] F. Iza and J. Hopwood, IEEE Trans. on Plasma Sci. **31**, 782 (2003).

[4] S. Belostotskiy, V. Donnelly, D. Economou, and N. Sadeghi, IEEE Trans. on Plasma Sci., to appear June 2009.

11:20am **PS2-TuM11 Experiment and Simulation Results of Limited Cathode Area MHCDs Operating in He**, ***R. Dussart***, Universite d'Orleans - CNRS, France, *T. Dufour,* Universite d'Orleans, France, *L.J. Overzet, M. Mandra, J.B. Lee, M. Goeckner,* University of Texas, Dallas, *L.C. Pitchford,* CNRS - Laplace, France, *N. Sadeghi,* LSP - CNRS, France, *P. Lefaucheux,* CNRS, France, *P. Ranson*, Universite d'Orleans, France

Micro Hollow Cathode Discharges (MHCDs) offer the unique property to create DC micro plasmas in a stable regime at atmospheric pressure [1]. In collaboration with UTDallas (Texas), micro reactors are elaborated by usual microtechnology techniques (sputtering, electrodeposition, lithography, …), usually used in microelectronics and MEMS technology. A first set of microcavities in alumina were prepared and tested in helium. Optical and electrical characterizations were carried out in different cases: single or several cavity devices and for a limited or not cathode area. V- I characteristics were plotted in the different configurations and for different experimental conditions. When the cathode area is limited, an abnormal glow regime can be obtained, which favors the initiation of the plasma in multiple cavities [2]. By adding a small amount of N_2 to the discharge, the gas temperature was determined by fitting the second positive system $C^3Õ_u$-$B^3Õ_g$ emission spectra using the software developed at the LSP at Grenoble (France). Simulations of a single MHCD with variable cathode surface area were also carried out using the 2D code developed in Toulouse [3]. Simulation results will be compared to the experimental data. Finally, by applying voltage ramps to the microdischarge, hysteresis effects were observed and will be also discussed.

[1] K. H. Schoenbach, R. Verhappen, T. Tessnow, P. F. Peterkin, W. Byszewski, « Microhollow cathode discharges » Appl. Phys. Lett. 68, 13 (1996)

[2] T. Dufour, R. Dussart, P. Lefaucheux, P. Ranson, L. J. Overzet, M. Mandra, J. B. Lee, M. Goeckner « Effect of limiting the cathode surface on direct current microhollow cathode discharge in helium » Appl. Phys. Lett., 93, 071508 (2008)

[3] J. P. Boeuf and L. C. Pitchford, K. H. Schoenbach, « Predicted properties of microhollow cathode discharges in xenon » Appl. Phys. Lett., 86, 071501 (2005)

11:40am **PS2-TuM12 Linear Microplasma Array using Strongly-Coupled Resonators**, ***J. Hopwood***, *Z. Zhang*, Tufts University

Instabilities in atmospheric pressure plasmas are responsible for the irreversible glow-to-arc transition of cold microplasmas into destructive arcs. DC microplasmas are usually stabilized using a ballast resistor. Alternatively, AC microplasmas are controlled by rapidly extinguishing the discharge through the electrical charging of dielectric barriers surrounding the electrodes (*i.e.*, the DBD). The negative differential resistance of the glow-to-arc region also makes parallel operation of plasmas difficult. Stable arrays of DC and AC microplasmas, however, are possible using distributed ballasting[1]. In this work, we stabilize the individual microplasma using a quarter-wave resonator constructed from a microstrip transmission line. As the microwave input power increases, the microplasma's electrical resistance drops and the resonator is automatically quenched; thus arcing is avoided. Microwave impedance spectroscopy measures the plasma resistance as a function of input power and confirms the negative differential resistance of the microplasma. The technical challenge to operate multiple microwave resonators is met by employing coupled-mode theory[2]. An array of high-Q resonators will couple energy efficiently among themselves provided that all resonators share a common resonance frequency. A single microwave power source (400 MHz, 4 watts) drives the first resonator in a linear array and the remaining undriven resonators redistribute the input energy such that multiple microplasmas operate in a stable, parallel manner. Solutions to the classic coupled-mode theory equations are compared with electromagnetic simulations of the resonator array and with the observed excitation of multiple microplasmas. Having confirmed that coupled-mode theory is applicable to microplasma arrays, we then demonstrate the production of stable, high density ($n_e > 10^{14}$ cm^{-3}) cold atmospheric pressure plasma in a linear configuration that is suitable for high-rate material processing.

[1] K. H. Becker, K. H. Schoenbach and J. G. Eden, J. Phys. D: Appl. Phys. **39,** R55 (2006).

[2] H. A. Haus and W. Huang, Proc. IEEE **19**, 1505 (1991).

Advanced Surface Engineering
Room: C4 - Session SE-TuM

Hard and Nanocomposite Coatings
Moderator: P.H. Mayrhofer, Montanuniversitat Leoben, Austria

8:00am **SE-TuM1 AlTiN and AlCrN Hard Coatings - Alloying as an Approach to Improve Oxidation and Tribological Properties**, ***C. Mitterer***, University of Leoben, Austria **INVITED**

Metastable transition metal aluminum nitride based hard coatings like AlTiN and AlCrN grown by plasma-assisted physical vapor deposition are nowadays widely used to protect high-performance tools against wear and oxidation. The excellent properties of these coatings arise from their ability to form protective Al_2O_3-based oxide scales and from the decomposition of their metastable face-centered cubic (fcc) lattice, resulting in age hardening.

The aim of this presentation is to give a survey of attempts to alloy AlTiN and AlCrN coatings, with the goals to improve hardness and wear resistance, oxidation resistance, toughness, and to reduce friction. Coatings were synthesized by reactive cathodic arc evaporation, and powder-metallurgically produced TiAl and CrAl targets with the alloying elements V, Si, B, Ta, and Ru have been used. Low Si, B and Ta contents are incorporated in the single-phase fcc solid solutions, enhancing both mechanical properties and oxidation resistance. In particular, for AlTiTaN coatings the onset temperature for oxidation is shifted to significantly higher values compared to AlTiN, which is related to a reduction of intrinsic stresses in the rutile layer formed underneath the top Al_2O_3 scale. B alloying of AlCrN results in the formation of a nanocomposite structure, with nanosized fcc grains surrounded by a BN-rich grain boundary layer, giving rise to extremely high hardness values and wear resistance. On the other hand, V alloying can be used to form self-lubricious V_2O_5 oxide layers, where their low friction coefficients in the temperature range between 550 and 700°C arise from liquid lubrication, due the low melting temperature of this phase. Furthermore, low contents of Ru have been shown to increase the toughness of AlTiN coatings, which is assumed to formation of a metallic Ru phase within these coatings.

In summary, alloying of metastable transition metal aluminum nitride based hard coatings enables to design advanced quaternary and multiternary hard coatings with property combinations meeting the requirements of severe machining processes.

8:40am **SE-TuM3 Pressure Dependence of the Al Ion Energy Distribution Functions during Filtered Cathodic Arc Thin Film Growth in an Ar, O_2 Ambient**, *A. Atiser, S. Mraz,* ***J.M. Schneider***, RWTH Aachen University, Germany

Charge state resolved ion energy distribution functions (IEDFs) of Al^+, Al^{2+} and Al^{3+} were measured as a function of Ar pressure in the range from 5.7×10^{-5} to 2.13 Pa (0.01 to 256 Pa cm). As the pressure distance product is increased, the annihilation of the Al^{2+} and Al^{3+} populations as well as the thermalization of the Al^+ ion population is observed, resulting in the formation of a close to monoenergetic beam of Al^+ ions at pressure distance product of 256 Pa cm. The average charge state was reduced from 1.58 to 1.00 as the pressure distance product was increased from 0.01 to 32 Pa cm. Thermalization is also observed in an Ar/O_2 mixture at 128 Pa cm, where stoichiometric γ -alumina films are grown. The IEDFs have been fitted by a shifted Maxwellian distribution. The plasma processing strategy presented here resulting in a monoenergetic Al^+ plasma beam may through substrate bias potential variations enable effective tailoring of thin film properties such as density, elasticity and phase stability.

9:00am **SE-TuM4 Al-Si-N Thin Films: Nanocomposites and Solid Solutions**, *A. Pélisson, M. Parlinska-Wojtan, H.J. Hug,* ***J. Patscheider***, EMPA, Switzerland

Thin films consisting of Al-Si-N were prepared by reactive magnetron sputtering from elemental targets in an Ar/N_2 reactive atmosphere at 200°C. The system shows a solubility limit for silicon at around 6 atomic %. Correspondingly the Al-Si-N system forms, as a function of the silicon content, either a solid solution or a two phase nanocomposite structure,. To understand the the properties and formation of the nanocomposite nanoscaled multilayers were used as a simplified model system. Coatings with a total thickness of about 1 micron and consisting of alternating layers of h-AlN or h-$Al_{1-x}Si_xN$ (5 nm) and a-Si_3N_4 (from 0.25 nm to 2.0 nm) were prepared. The hardness as well as the residual stress state are strongly influenced by the thickness of the Si_3N_4 layer and the silicon content of the crystallineAl-Si-N layer. Maximum hardness values of 33 GPa are reached for a Si_3N_4 layer thickness of 0.35 nm, whereas the stress state can be tuned between – 1.5 and + 1.5 GPa. Both High Resolution TEM and XRD showed that, for Si_3N_4 layer thicknesses below 1 nm, the Si_3N_4 layers grow heteroepitaxially on AlN. The implication for the hardness of isotropically deposited solid solution and nanocomposite thin films of Al-Si-N will be discussed.

9:40am **SE-TuM6 Development of Water Repellent Metal Oxide Thin Film as Like Organic Polymer**, ***T. Watanabe***, *Y. Yokota, N. Yoshida,* The University of Tokyo, Japan, *Y. Okura*, Kogakuin University, Japan

Mechanically durable water repellent thin film composed of only metal oxides such like Al_2O_3, HfO_2, ZrO_2, TiO_2 and CeO_2 were successfully developed by sol-gel process. The key points to enhance dynamic hydrophobicity are reducing surface roughness and increasing chemical homogeneity. Surprisingly to say, developed films show 100 degree of water contact angle and sliding angles of water droplet is only around 20 degree. Water repellency has not been deteriorated even by 500 times abrasion tests of 0.1kg/cm^2. Water removability on these films is as like that of hydrophobic polymer surface. Fundamentally, intrinsic surface wettability of metal oxide is hydrophilic. However nanometer scale flatness and homogenous surface reduce activation energy of de-wetting process of water droplet. It is considered to cause of higher water removability. Durable hydrophobic surface composed only by inorganic oxide attracts much attention because it can be applied for water repellent automobile glass window and other applications which need higher mechanical strength and durability. Moreover, developed films show several unique properties which cannot be observed on organic polymer surfaces.

11:00am **SE-TuM10 Anti-Wear and Anti-Bacteria Behaviors of Rejuvenated TaN-Cu Nanocomposite Thin Films**, ***J.H. Hsieh***, *P.C. Liu,* Ming Chi University of Technology, Taiwan, *C. Li*, Nanyang Technological University, Singapore

TaN–Cu nanocomposite films were deposited by reactive co-sputtering on Si and tool steel substrates. The films were then annealed using RTA (Rapid Thermal Annealing) at 400 °C for 2, 4, 8 minutes respectively to induce the nucleation and growth of Cu particles in TaN matrix and on film surface. Cu nano-particles emerged on the surface of TaN-Cu thin films were then removed after the samples were tested for their anti-wear and anti-bacterial behaviors. The samples were then re-annealed (rejuvenated), and re-tested for their anti-wear and anti-bacterial behaviors. The results reveal that the rejuvenated samples could have similar anti-wear and anti-bacterial behaviors so long as the annealing conditions were well adjusted. However, the hardness of the samples would decrease to a certain extent.

Surface Science
Room: M - Session SS1-TuM

Oxide Surfaces: Reactions and Structure
Moderator: R.L. Kurtz, Louisiana State University

8:00am **SS1-TuM1 UV Induced Work Function Change of Oxide Surfaces**, ***S. Gutmann***, *M. Wolak, M. Conrad, M.M. Beerbom, R. Schlaf*, University of South Florida

The work function of conductive oxide thin films is an important parameter determining the band line-up at interfaces to active electronic materials in optoelectronic devices. The presented experiments aimed at the measurement of the work function of indium tin oxide (ITO), and nanocrystalline TiO_2 and ZnO thin films using photoemission spectroscopy. Traditionally, ultraviolet photoemission (UPS) is used to measure the work function of solid surfaces by means of the photoelectric effect. Such measurements are able to yield absolute work function values.

Our experiments showed that UPS measurements reduce the work function of oxide surfaces by up to 0.5 eV. This effect occurs within seconds, effectively preventing measurements of the 'true' work function of surfaces prior to UV exposure. A similar effect is observed when exposing oxide surfaces to x-ray doses typical for x-ray photoemission spectroscopy measurements. It was possible to quantify these effects through the use of low intensity XPS (LIXPS) based work function measurements, which allow a time-window sufficiently long for work function measurements without significantly influencing the work function. The experiments suggest that the work function reduction occurs through the hydroxylation of oxygen vacancies in the oxide surfaces by means of photochemical dissociation of adsorbed water molecules.

8:40am **SS1-TuM3 Low-energy Alkali Ion Scattering Studies of Bi2Sr2CaCu2O8+δ**, ***R.D. Gann***, University of California, Riverside*, J. Wen, Z. Xu, G.D. Gu,* Brookhaven National Laboratory*, R.Q. Wu,* University of California, Irvine*, J.A. Yarmoff*, University of California, Riverside

The high-T_c cuprate BSCCO-2212 is investigated with low energy (0.5-10 keV) alkali ion scattering, which is an extremely surface-sensitive technique that can reveal compositional, structural and electronic information about a surface. Samples were cleaved at liquid nitrogen temperature in ultra-high vacuum, and time-of-flight spectroscopy was used to measure charge-resolved energy spectra of the scattered ions. Clean surfaces were shown to be terminated by BiO, and the inhomogeneous surface potential of the as-cleaved surface was revealed by the angular dependence of the neutralization. The effect on local potential due to adsorption of alkali and halogen species was ascertained by neutralization measurements and verified with density-functional theory. Deliberate damage induced by 500 eV argon sputtering revealed a gradual disordering of the surface as underlying metallic species diffuse upward, rather than layer-by-layer etching, as earlier SIMS studies have suggested. A detailed view of the surface termination opens the door for studies of other, similarly layered materials such as Bi_2Se_3.

9:00am **SS1-TuM4 Termination and Identification of Surface Species on the Magnetite (111) Surface Studied by Scanning Tunneling Microscopy**, ***T.K. Shimizu***, *Y. Kim,* RIKEN, Japan, *M. Kawai*, RIKEN and University of Tokyo, Japan

Besides its magnetic properties, magnetite exhibits an interesting first order phase transition called the Verwey transition (T_V~120 K). Although there have been many atomistic investigation using scanning tunneling microscopy (STM) at room temperature (RT), the most stable structure of Fe_3O_4(111) has not been yet in complete agreement. By employing STM and scanning tunneling spectroscopy (STS) at 77 K, we have studied the Fe_3O_4(111) surface using a naturally grown single crystal. STM images show a hexagonal lattice with an approximately 0.6 nm periodicity, no remarkable difference from RT observations. Based on the comparison of STS with a theoretical calculations, this surface can be assigned to the Fe_{tet} termination, where the layer of Fe cations at the tetrahedral site terminates the crystal, supporting results of several early studies. In addition to these findings, we found two distinct features on the as-prepared surface. These features are considered to be the same species as those seen in the RT STM study [1] from the site and the bias dependence of their appearances. We were able to obtain direct evidence of their origin being water by intentionally adsorbing water both at 77 K and at RT, in agreement with previous predictions [1]. For instance, by injecting tunneling electrons into as-dosed intact water molecules at 77 K, we could induce reactions to one of the originally observed species. In contrast to RT experiment, however, their diffusion requires much higher energy, which may be explained by the inefficient electron-phonon (e.g., OH stretching mode) coupling due to the smaller number of electronic states available near the Fermi level below the Verwey transition temperature.

[1] Sh. Shaikhutdinov and W. Weiss, J. Mol. Catal. A: Chem. 158, 129-133 (2000)

9:20am **SS1-TuM5 Scanning Tunneling Microscopy Investigation of the Vanadium Dioxide Surface and Its Related Metal-Insulator Transition (MIT)**, ***W. Yin***, *P. Reinke*, *S. Wolf*, University of Virginia, *C. Ko*, *S. Ramanathan*, Harvard University

Vanadium dioxide (VO_2) is one of the most interesting thermochromic materials exhibiting a metal-insulator transition (MIT) close to room temperature ($T_{MI} \approx 340$ K). This study presents an observation of the progression of the MIT with scanning tunneling microscopy and spectroscopy as a function of temperature with high spatial resolution. The high-quality VO_2 thin films used in this study were deposited on (0001) Al_2O_3 substrates using a sputtering technique. Electron tunneling current (conductivity) maps showed that the material surface was semiconducting before heating, and highly metallic above T_{MI}. The spatial distribution of bandgaps, semiconducting and metallic regions, is compared to the sample topography, and a model describing the progression of the MIT across the surface will be presented. In particular, the role of the chemical modification and reduction of the surface during heating will be discussed, and compared to the stability of the bulk phase. The surface was still partially metallic after cooling down but tended to recover its semiconducting nature over a long period of time. We attribute such irreversible surface electrical changes to the loss of oxygen and the strain relaxation in the VO_2 lattice. The spatial distribution of bandgaps indicates that the phase transition probably started from grain boundaries and the VO_2 surface exhibited an inhomogeneous behavior both above T_{MI} and after heat treatment.

9:40am **SS1-TuM6 The Adsorption and Reaction of Alcohols on Poorly Crystalline γ–Al_2O_3 Surfaces**, *J. Kwak*, *J. Szanyi*, ***C. Peden***, Pacific Northwest National Laboratory

γ-alumina, one of the metastable 'transition' alumina structural polymorphs, is an important catalytic material both as an active phase and as a support for other catalytically active phases, with widespread applications ranging from petroleum refining to automotive emission control. As such, the bulk and surface structure of γ-alumina, and its formation and thermal stability have been and continue to be the subject of a considerable amount of research, including attempts to prepare model surfaces via the controlled oxidation of NiAl alloy single crystals. However, due to the low crystallinity and very fine particle size of γ-alumina, it is very difficult to apply well-established analytical techniques for determining its surface structures. Of particular importance for understanding the catalytic properties of γ-alumina, relating its surface structure to the origin of Lewis and Brönsted acidity has been of considerable interest and has been studied by solid state NMR and FTIR spectroscopies, and most recently by theoretical calculations. In this presentation, we describe recent studies using ultra-high resolution NMR spectroscopy as an especially useful probe of the γ-alumina surface structure, and its relevance to catalytic behavior. In particular, we coorelate the NMR spectra with measurements of the adsorption and reaction of alcohols. In this way, we demonstrate a strong dependence of this chemistry on the presence of specific 5-coordinate Al^{3+} ions. These sites, in turn are a function of the dehydration temperature of the alumina material before use. From these correlations, we are able to explain a considerable number of prior observed phenomena.

10:40am **SS1-TuM9 The Growth and Structure of Ceria Islands on Cu(111)**, ***F. Yang***, *J. Graciani*, *S. Senanayake*, *J.B. Park*, *D.J. Stacchiola*, *P.J. Liu*, *J. Hrbek*, *J.A. Rodriguez*, Brookhaven National Laboratory

Ceria-based catalysts are widely used for a number of catalytic reactions, such as the water gas shift reaction ($CO + H_2O \rightarrow H_2 + CO_2$) or CO oxidation ($CO + {}^1/_2\, O_2 \rightarrow CO_2$). Recently, it has been reported that ceria nanoparticles supported on Au(111) are much more efficient for the water gas shift reaction than the oxide or metal alone. In this work, we investigate the CeO_x/Cu(111) system as a model for Cu-CeO_2 water-gas shift catalysts. Using scanning tunneling microscopy (STM), we study the nucleation and growth of ceria islands on the Cu(111) surface. Ce is vapor-deposited on Cu(111) under an atmosphere of O_2 (~ 1×10^{-7} Torr) at different temperatures (300-600 K). We show how the geometric structures of ceria islands could be changed by altering the growth kinetics. We also show the evolution of the morphology when the CeO_x/Cu(111) surface interacts with CO or H_2O. Through an interplay with density functional theory (DFT) and X-ray photoelectron spectroscopy (XPS), the structure of supported ceria islands will be described.

11:00am **SS1-TuM10 Morphology and Electronic Structure of Ultrathin Oxide Films on $Pt_3Ti(111)$**, ***M. Moors***, *S. Le Moal*, *C. Becker*, *K. Wandelt*, University of Bonn, Germany

TiO_2 supported metal catalysts are known to have interesting catalytic properties, e.g. for oxygen reduction of water in fuel cells and for CO hydrogenation. The formation of titanium oxides on Pt-Ti alloy surfaces is one promising approach to develop new TiO_2 based model catalysts. In this work the crystallographic and electronic structure as well as the surface composition of ultrathin titanium oxide films grown on a $Pt_3Ti(111)$ single crystal surface have been investigated as a function of oxidation temperature (700 K to 1000 K) and oxygen exposure (up to 9000 L) using Low Energy Electron Diffraction (LEED), Ultraviolet Photoelectron Spectroscopy (UPS) and Auger Electron Spectroscopy (AES). The composition of the titanium oxide films formed on this alloy surface strongly depends on the preparation conditions. From AES and LEED measurements two different stable oxide phases have been identified at high temperatures (above 900 K), depending on the oxygen exposure. At lower oxygen exposures (below 135 L) the most stable structure is a quasi-hexagonal one (a = 3.35 Å, b = 3.25 Å, α = 124°) rotated by 4° with respect to one of the substrate symmetry axes. The p(2×2) pattern, which is attributed to the $Pt_3Ti(111)$ substrate, is still visible after this mild oxidation; suggesting that some areas of the substrate remain unoxidized. At higher oxygen exposures (between 220 L and 9000 L) the predominant structure is a commensurate hexagonal structure (a = 3.20 Å) rotated by 4° with respect to one of the substrate symmetry axes. In this case the p(2×2) substrate structure is no longer visible. Apart from these two stable structures, several additional LEED patterns have been observed, which are related to metastable oxide structures. However, this great diversity of LEED patterns is not reflected in the UPS measurements. Comparing the clean $Pt_3Ti(111)$ surface with Pt(111) shows a significant broadening of the Pt related intensity between 1 and 4 eV as well as the appearance of a strong Ti related signal around 6 eV. For the clean $Pt_3Ti(111)$ surface a work function of 5.02 eV has been determined. Oxidizing the alloy leads to additional peaks at a binding energy of 5.5 and 7.5 eV. The work function of the oxidized surface is increased by 0.3 eV related to clean $Pt_3Ti(111)$. Remarkably, neither the spectral shape nor the work function significantly depends on the temperature and oxygen pressure used during oxidation.

11:20am **SS1-TuM11 Facile C-H Bond Cleavage of Propane on a PdO(101) Thin Film**, ***J.F. Weaver***, *C. Hakanoglu*, *S.P. Devarajan*, *A. Minter*, University of Florida

Palladium oxide (PdO) is an excellent catalyst for the oxidation of alkanes under oxygen-rich conditions, but difficulties in preparing well-defined surfaces have hindered fundamental studies of PdO surface chemistry. We have recently found that a high-quality PdO(101) thin film can be grown on Pd(111) in ultrahigh vacuum by oxidizing the metal at moderate temperature using an oxygen atom beam. In this talk, I will discuss recent results showing that propane adsorbs into a strongly-bound molecular state on PdO(101) and undergoes facile C-H bond cleavage below 200 K. The adsorbed hydrocarbon fragments are completely oxidized by the PdO surface above about 400 K, yielding gaseous CO_2 and H_2O during temperature-programmed experiments. From measurements of product yields as a function of the surface temperature, we show that the initial C-H bond cleavage of propane on PdO(101) occurs by a precursor-mediated mechanism with a negative, apparent activation energy, and present evidence that the strongly bound molecular state serves as the precursor to the initial dissociation. We suggest that a donor-acceptor interaction between a C-H bond(s) of the propane molecule and a coordinatively unsaturated Pd atom enhances the binding of propane on PdO(101), beyond that expected for physisorbed molecules, and facilitates C-H bond activation. Finally, I will summarize recent experimental and computational results which show that CH_4 and H_2 molecules also interact strongly with PdO(101) through dative bonding. The activation of propane on PdO(101) is analogous to alkane reactions with mononuclear transition metal compounds for which alkane sigma complexes act as key intermediates.

11:40am **SS1-TuM12 Investigation of Oxygen Embedment and Surface Restructuring on the Cu(100) Surface by Density Functional Theory Calculations**, ***M. Lee***, *A. McGaughey*, Carnegie Mellon University, *J. Ren*, *J.C. Yang*, University of Pittsburgh

When the oxidation of a Cu(100) surface reaches 0.5 monolayer (ML) oxygen coverage, the surface structure transforms into the missing-row reconstruction. With further oxygen exposure, cuprite (Cu2O) islands nucleate and then grow both into and along the surface. To investigate the early stages of Cu(100) oxidation, we apply density functional theory calculations to study the oxygen embedment into the surface using the nudged elastic band (NEB) method. We find that as the surface oxygen coverage increases on the unreconstructed Cu(100) surface, the energy barrier for embedment decreases and the oxygen embedment is energetically favorable at coverages of 0.75 ML and 1.0 ML. At 0.5 ML coverage, the em- bedment energetics vary with surface morphology [c(2x2), missing-row reconstruction, and c(2x2) with 0.25 ML disordered vacancy structures], but in all cases the embedment is not energetically favorable. At 0.625 ML coverage, however, the oxygen embedment is favorable and we investigate the energetics for embedment into the missing row reconstruction through the missing row and alternate paths. We find that oxygen embedment through the missing row is more probable. We predict that oxygen sub-surface diffusion will occur because the energy barrier is comparable to that for surface diffusion. To study the intermediate states between the missing-row reconstruction and cuprite island nucleation, we are investigating various combinations of on- and sub-surface oxygen adsorbed structures by DFT calculation. We find that an additional oxygen molecule plays a role in the surface restructuring not only morphologically but also energetically for the unreconstructed Cu(100) surface. We are using a similar methodology to investigate the role of the additional oxygen molecule for surface restructuring on the missing-row reconstructed surface.

Surface Science
Room: N - Session SS2-TuM

Reactions on Metals and Bimetallics
Moderator: S. Chiang, University of California, Davis

8:00am **SS2-TuM1 Surface Structure of the Pd-H System**, ***K.F. McCarty***, Sandia National Laboratories, *B. Santos*, Universidad Autónoma de Madrid, Spain, *T. Herranz*, Intituto de Química-Física "Rocasolano", Spain, *J.I. Cerda, J.M. Puerta*, Instituto de Ciencias de Materiales de Madrid, Spain, *J. de la Figuera*, Intituto de Química-Física "Rocasolano", Spain

Palladium hydride, PdH, is the model transition-metal hydride. Surface-science studies of PdH are scarce for two reasons. First, hydrogen pressures in the 10's of torr range are needed to form PdH near room temperature. Second, the expansion of the lattice that occurs during hydride formation tends to destroy Pd single crystal. To overcome this latter problem, we use thin epitaxial films of Pd(111) on Ru(0001) and W(110) to examine the surface science of the Pd-H system. To achieve an effective higher hydrogen pressure, we expose the Pd films to atomic H. We use low-energy electron diffraction (LEED) to characterize the Pd surface after H exposure. By performing the LEED in a low-energy electron microscope (LEEM), we are able to collect diffraction data from the same, atomically flat regions before and after H exposure. Detailed analysis of the LEED IV curves shows that exposure to atomic H at about 200K expands the interlayer spacing of the top two Pd layers but does not affect deeper layers. We interpret these changes as the formation of a surface hydride. Exposure to atomic H while cooling from above room temperature also produces the surface hydride. The lack of diffusion deeper into the film suggests that an energy barrier inhibits diffusion past the second Pd layer. The synthesis of a bulk hydride was attempted by exposing a Pd film to 40 torr of hydrogen and then reducing the pressure after cooling. The resulting material presented sharp, 3-fold diffraction patterns with an IV response different than the surface hydride. We will discuss the structure of this material, which we tentatively assign to a bulk PdH.

8:20am **SS2-TuM2 Surface-catalyzed O2 Adsorption on Quantum Thin Films**, ***J. Kim***, *A. Khajetoorians*, The University of Texas, Austin, *W.G. Zhu, Z.Y. Zhang*, Oak Ridge National Laboratory, *C.K. Shih*, The University of Texas, Austin

Pure crystalline Pb is well known to be inert with respect to oxygen gas. By using scanning tunneling microscopy we demonstrate that the oxygen adsorption on Pb films is greatly increased by Cs adsorbates acting as catalysts. Our previous studies show that Cs atoms can be easily incorporated into the surface layer of thin Pb films through a substitutional process when they are evaporated at low temperature (100 – 120 K). In addition, this Cs-Pb surface alloying process works cooperatively with the quantum size effect, leading to formation of nano-islands. This study explores the effect of the surface alloying on the oxidation. With only a minute concentration of Cs (0.004 ML coverage), we found a great enhancement of surface oxidation rates. Theoretical DFT calculations have revealed that the oxygen adsorption energy is greatly enhanced at the Cs substitutional sites. Subsequent oxygen exposures lead to great enhancement of oxidation which can be identified as PbO. Furthermore, we have explored the effect of temperature on the formation of Cs-Pb alloy and its consequences for the oxidation of Pb.

8:40am **SS2-TuM3 Surface Reactions on Model Gold Catalysts**, ***C.B. Mullins***, University of Texas at Austin **INVITED**

We have studied model gold catalysts consisting of gold clusters supported on planar titania supports and Au single crystalline samples employing standard UHV surface chemical probes in addition to molecular beam techniques. In this talk I will focus on our results relating to enhanced CO oxidation by adsorbed water and the oxidation of alcohols employing single crystalline bulk gold. Briefly, we have found that adsorbed water can greatly enhance CO oxidation on oxygen pre-covered bulk gold at low temperatures. Additionally, we have found that atomic oxygen pre-covered Au(111) can partially oxidize ethanol, 1- and 2-propanol, and 2-butanol to their respective ketone or aldehyde with high efficiency and selectivity.

9:20am **SS2-TuM5 Oxidative Removal of Carbodiimide (NCN) and Isocyanate (NCO) Species from Cu(001) Surfaces**, ***E.Z. Ciftlikli***, *J. Lallo, E.Y.-M. Lee, S. Rangan, L. Tskipuri, R.A. Bartynski, B.J. Hinch*, Rutgers University

Adsorbed isocyanate (NCO) species on Cu(001) undergoes oxidation, in the presence of $O_{(a)}$, at temperatures as low as 373K. $N_{(a)}$ remains and $CO_{2(g)}$ evolves. On the other hand, a NCO/Cu(001) surface, in the absence of any other coadsorbates, is stable up to ~523K. Above this temperature, a bimolecular decarboxylation reaction is induced, which produces $CO_{2(g)}$ and a surface bound carbodiimide (NCN) species alone. RAIRS measurements confirm a surface parallel species with an "sp" hybridized carbon atom. The introduction of oxygen at room temperature on NCN/Cu(001) leads to the reappearance of NCO species on the surface. The apparent yield of reformed NCO is not simply in proportion to the initial NCO dose levels. The chemistry of the NCO species is affected by the likely coadsorbates; $N_{(a)}$, $O_{(a)}$, and $NCN_{(a)}$. The ν_a(NCO) bands observed in RAIR spectra of these partially oxidized surfaces, apart from being complex in shape, display a significant blue shift with respect the ν_a(NCO) modes observed when similar quantities of NCO are adsorbed on coadsorbate-free surfaces. In addition, the annealing of these surfaces to 473K indicates only a partial further oxidation of NCO. Even at excessive O_2 doses, NCO is not fully oxidized by 473K. A further annealing to ~ 623K is required for complete NCO removal. We will discuss the possible factors that limit NCO oxidation in these surfaces.

9:40am **SS2-TuM6 Kinetics of HCN Decomposition and CNH_2 Formation on Pt(111)**, ***X. Hu***, *M. Trenary, R.J. Meyer*, University of Illinois at Chicago

The kinetics of HCN (hydrogen cyanide) decomposition to H and CN and the subsequent hydrogenation of CN to the CNH_2 species on the Pt(111) surface were studied with time-resolved reflection absorption infrared spectroscopy (RAIRS). The use of RAIRS for kinetic studies can uniquely provide important information on the mechanisms of surface reactions, particularly when these reactions occur below the temperature at which products desorb from the surface. In addition, from the analysis of kinetic data, activation energies for elementary surface reactions on well-defined systems can be determined and thereby provide important experimental benchmarks for comparison with the results of state-of-the-art theoretical calculations. Hydrogen cyanide adsorbs on Pt(111) at a temperature of 85 K to give an intense CH stretch vibration at 3300 cm^{-1}. The time dependent decrease of this peak was monitored at temperatures between 120 and 135 K, the temperature range where the C-H bond of HCN breaks. The decrease in CH stretch peak intensity appears to follow first order kinetics and is attributed to both C-H bond breaking and HCN desorption. The CNH_2 species is characterized by RAIRS peaks at 3370 cm^{-1} (N-H stretch), 1566 cm^{-1} (NH_2 scissors), and 1324 cm^{-1} (C-N stretch). The increase in coverage of the CNH_2 species was monitored by following the time dependence of the 1566 cm^{-1} peak, the most intense mode of CNH_2, in the temperature range of 210 to 230 K. The CNH_2 formation rate is found to follow second order kinetics. The spectra show the appearance of an intermediate species with a peak at 3347 cm^{-1}, the intensity of which initially increases with time, reaches a maximum, and then decreases as CNH_2 is formed. This peak is identified as the N-H stretch of an HNC surface intermediate. Through kinetic modeling of the time dependence of the coverages of the HCN, HNC, and CNH_2 species, rate constants were derived at each temperature and activation energies were obtained from Arrhenius plots. The experimental results were then compared with the results of density functional theory (DFT) calculations on the stability and structures of the intermediates. Activation barriers for each step of the reaction were also obtained from the DFT calculations. The calculations confirm that CNH_2 is the energetically favored product of the reaction and that CNH_2 has the structure implied by the RAIR spectra. The calculations also predict that HNC is a stable surface intermediate. However, the structures of both adsorbed HCN and HNC as implied from the RAIRS data disagrees with the optimized structures obtained from the DFT calculations.

10:40am **SS2-TuM9 Surface Segregation on Composition Spread Alloy Films**, ***A.J. Gellman***, *J.B. Miller, D. Priyadarshini*, Carnegie Mellon University

Surface segregation has been studied in Pd_xCu_{1-x} alloys used for hydrogen purification membranes. Surface segregation influences the performance of these alloys for hydrogen purification and furthermore, segregation at the surfaces of these materials is a sensitive function of the concentration of contaminants such as sulfur. Segregation is not just restricted to the topmost atomic layer of the alloy. The concentration of one component in the top few layers of the surface may differ from that of the bulk. Because surface segregation is a continuous function of bulk composition, x, a complete understanding of segregation in a binary alloy requires the development of high throughput methods that allow concurrent measurements of surface segregation at all possible values of bulk composition.

Surface segregation has been studied in a $Pd_{70}Cu_{30}$ alloy using both x-ray photoelectron spectroscopy (XPS) and low energy ion scattering (LEIS). The results show that the topmost atomic layer is rich in Cu. On the other hand, the near-surface region consisting of the immediate subsurface layers is rich in Pd. Furthermore, the adsorption of sulfur on the surface causes the complete elimination of Cu from the topmost layer.

A high throughput method for study of surface segregation has been developed that is based on the deposition of thin Composition Spread Alloy Films (CASFs) that contain all possible bulk compositions of the Pd_xCu_{1-x} alloy. Spatially resolved surface analysis of the surface of the Pd_xCu_{1-x} CASF has been achieved using XPS. The results show that the near-surface region of the alloy is Pd rich over a wide range of bulk Pd concentrations.

11:00am **SS2-TuM10 Catalytic Hydrogenation of Butadiene on Bimetallic Surfaces**, *M. Moors,* ***C. Breinlich,*** University of Bonn, Germany, *T. Kobiela,* Warsaw University of Technology, Poland, *C. Becker, K. Wandelt*, University of Bonn, Germany

Investigations of bimetallic systems with regard to their surface composition, morphology and adsorption properties for reactive gases are essential for the development of new catalysts with higher efficiency and durability. An interesting catalytic reaction is the partial hydrogenation of butadiene to 1-butene without complete hydrogenation to butane and the coking of the catalyst due to decomposition of the educt. In this work the hydrogenation of butadiene has been investigated on bimetallic Sn-Pd(111) and Au-Pd(111) surface alloys by means of Ultraviolet Photoelectron Spectroscopy (UPS) and Temperature Programmed Desorption (TPD). The bimetallic surfaces were prepared by depositing Sn or Au onto a clean Pd(111) surface followed by controlled annealing. Annealing an at least 4 ML thick Sn film to 750 K results in an ordered p(2x2) Pd_3Sn surface alloy as evidenced by Low Energy Electron Diffraction (LEED). Further annealing to 850 K leads to the formation of the thermodynamically more stable $(\sqrt{3}x\sqrt{3})R30°$ Pd_2Sn surface alloy. After annealing to 1000 K all Sn has diffused into the Pd(111) substrate. No ordered alloy phase has been found for the Au-Pd system. Annealing to temperatures gradually higher then 450 K leads to a continuous decrease of the Au surface concentration until at 1050 K Au has completely disappeared into the bulk. Under UHV conditions the Sn-Pd(111) alloy surfaces exhibit a lower hydrogenation rate of butadiene in comparison to the pure Pd(111) surface. The butene production strongly decreases with increasing Sn amount at the surface. This decreasing reactivity, however, is accompanied by an increasing selectivity and decreasing coking of the surface. Alloying Pd with Au on the other hand results in a significantly improved reactivity towards butene compared to pure Pd(111), while the selectivity is only slightly decreased. Furthermore, the coking of the Au-Pd(111) surface is even lower than observed on pure Pd(111), which makes this system a promising hydrogenation catalyst.

11:20am **SS2-TuM11 Buffer Layer Assisted Deposition of Pb-Au Bimetallic Nano-clusters: Characterization and Chemical Reactivity**, ***M. Asscher***, Hebrew University of Jerusalem, Israel

Control over size and density of metallic nano-particles on oxide surfaces is important for studying model heterogeneous catalysts.

We have deposited metallic clusters on model SiO2 / Si(100) support, assisted by amorphous solid water (ASW) as a buffer. One may control this way the average size and density of metallic clusters independently by changing the ASW layer thickness, metal dosage and then repeat the deposition process. Bimetallic Pd-Au clusters were prepared this way and characterized by IR spectroscopy, AFM, SEM and TEM measurements in order to determine their structural and crystalline nature.

Directly deposited pure Pd clusters, 5±2 nm diameter, were found reactive in acetylene trimerization to benzene. The buffer assisted Pd-Au bimetallic clusters in comparison, are at least three times more reactive than the pure Pd, in spite of having smaller surface density of Pd atoms. Acetylene hydrogenation to ethylene was also studied. This product is two orders of magnitude more probable than benzene. Once again the bimetallic alloy was significantly more reactive than the pure Pd. Clean gold clusters were totally inactive. Preliminary results reveal the effect of pre-annealing to temperature below 300K, suggesting strong sensitivity to sintering. The possibility of size dependent reactivity will be discussed.

11:40am **SS2-TuM12 Theoretical Prediction of Ordering and Reactivity of Bimetallic Gold Alloy Surfaces**, ***J. Stephens***, *H. Ham, G. Hwang*, University of Texas at Austin

Bimetallic materials have shown great promise for the development of superior catalysts. The recent surge of new interest in catalysis by gold has led researchers to investigate the effects of adding gold to other metals. While mechanisms underlying the alloying effect are still not understood in detail, recent evidence suggests that the enhanced reactivity of bimetallic catalysts can be attributed to a combination of metal-metal interactions (ligand effect) and unique mixed-metal surface sites (ensemble effect). The ability to accurately predict the arrangements of constituent atoms in a surface alloy is indispensable to unraveling the roles played by the ensemble and ligand effects in the performance of bimetallic model catalysts. We might expect that the arrangement of surface and near-surface atoms is a complex function of temperature, stoichiometric ratio, and surface facet, but thus far, only very limited theoretical effort has been undertaken to determine the atomic distribution of bimetallic alloys. We have developed a scheme to predict the equilibrium arrangement of atoms in surface alloys at finite temperatures. Our scheme is based on the Ising model, and is capable of reproducing DFT-predicted total energies to within no more than a few meV per surface atom. We will present our scheme in detail, as well as what we have learned about the effects of temperature, composition, surface facet, and particle identity on the arrangement of surface atoms for various gold-based binary alloys including gold-palladium and gold-platinum. We will also discuss how the atomic arrangements affect the reactivity of gold-based alloy surfaces particularly towards oxidation of hydrogen and carbon monoxide.

Thin Film
Room: B3 - Session TF1+SE-TuM

Glancing Angle Deposition I
Moderator: T. Karabacak, University of Arkansas at Little Rock

8:00am **TF1+SE-TuM1 Nanorod Structures for Energy Conversion**, ***N.A. Koratkar***, Rensselaer Polytechnic Institute **INVITED**

Oblique angle deposition (OAD) is a technique which allows for fabrication of unique nanostructures, which cannot be grown by advanced lithographic techniques. OAD is simple, fast, cheap, has high mass production capability and can generate unique two- and thee-dimensional nanostructures with large aspect ratio and controllable porosity, shape and symmetry. The fact that these nanostructures can be integrated onto a substrate platform makes them practical for many realistic applications. In this talk I will demonstrate the application of nanorods grown by OAD in various key device applications of today's energy starved society. The first is nanostructured Si anodes for rechargeable Li-ion batteries with higher capacity. The second is the development of Zinc Oxide (ZnO) and Indium Tin Oxide (ITO) nanorods by magnetron sputtering at low temperatures and their use as enhanced transparent conducting electrodes for polymeric photovoltaic cells. The third is the use of Pt nanorod based electrode architectures for proton exchange membrane fuel cells and the fourth is the use of Cu nanorods architectures for enhanced nucleate boiling which has strong implications for the management of thermal energy.

8:40am **TF1+SE-TuM3 Nanophotocatalysts Engineered by Glancing Angle Deposition Method**, ***W. Smith***, *Y. Zhao*, University of Georgia

TiO_2 has long been used as an efficient and effective photocatalyst material, with applications in water purification, water splitting for hydrogen generation, clean windows, and many others. The photocatalytic efficiency of TiO_2 can be enhanced by increasing its surface area as well coupling it with another semiconductor which can create a charge separation effect. There are many methods to produce high surface area nano-sized TiO_2 such as sol-gel, hydrothermal, and ball-milling, but these techniques are governed by surface chemistry and random aggregation, and are difficult to control the overall size and morphology of the nanoparticles. These issues can be fixed by utilizing an oblique angle deposition (OAD) technique and glancing angle deposition (GLAD) technique, that can create ordered nanorod arrays with tunable height, separation, density and heterostructures. With these unique advantages, we systematically studied the photocatalytic rate of methylene blue versus the TiO_2 nanorod height, and found a scaling relationship that can be interpreted by a surface reaction model. We also created WO_3-TiO_2 two-layer thin film, tilted nanorods, and vertical nanorods by e-beam deposition, OAD, and GLAD. Two important factors played a role in the observed photocatalytic properties; the crystal phase of each material, and the interfacial area between TiO_2 and WO_3. The best sample was found to be the GLAD multi-layer nanorod array, which showed an enhancement up to 3 times over single layer TiO_2 GLAD nanorods. The GLAD structure had a higher interfacial area between TiO_2 and WO_3 than other samples. To maximize the interfacial area between the two materials, a dynamic shadowing growth (DSG) method was used to create a core-shell nanorod array. WO_3 nanorods were first grown on a bare substrate using GLAD to serve as the "core". A TiO_2 "shell" was then deposited such that the entire WO_3 "core" nanorod was covered. The photocatalytic decay rate for these core-shell samples again showed further improvement over single layer TiO_2 thin films and multi-layer c-TiO_2/a-WO_3 films by 13 and 3 times respectively.

These results show that the GLAD based nanofabrication technique is a versatile tool to design new photocatalytic nanostructures. With more structural and material engineering, better photocatalyst structures can be engineered.

9:00am **TF1+SE-TuM4 Enhanced Optical Absorption and Photoconductivity Response of Indium Sulfide Nanorod Arrays**, ***M.F. Cansizoglu***, *T. Karabacak, H.W. Seo,* University of Arkansas at Little Rock*, R. Engelken*, Arkansas State University

Indium (III) sulfide is a wide bandgap and photoconductive material that has attracted attention due to its potential applications in optical sensors and in photovoltaic devices. High optical absorption in active regions of these devices is one of the key parameters that determine their performance especially in solar cell and photodetector applications. In this study, we show that indium sulfide nanorod arrays deposited by glancing angle deposition (GLAD) technique have superior optical absorption and low reflectance properties compared to conventional flat thin film coatings. Our GLAD nanorods had about 96% absorption in the sub-600 nm spectrum, while much thicker and denser thin films of indium sulfide was able to absorb only 80% of the incident light in the same spectrum. Due to the high optical absorption, a significant photoconductivity response was also observed in the nanorod samples, whereas no measurable photoresponse was detected in conventional thin films. In addition, we give a preliminary description of the enhanced light absorption properties of the nanorods by using Shirley-George Model that predicts enhanced diffuse scattering and reduced reflection of light due the rough morphology.

9:20am **TF1+SE-TuM5 Oblique Angle Polymerization**, ***M.C. Demirel***, Penn State University

The growth of spatially organized structures is of considerable fundamental interest, since it may provide us with important clues to the way in which organized structures form in Nature. A closer look at complex structures in insect wings and lizard toes reveal organized structured features at the microscopic scale. The organized structures in Nature are formed through evolutionary processes, and these complex molecules and features are built using molecular protein machinery. Synthetic polymers, that mimic biological materials in their designs, form organized structures too. We have demonstrated that nanostructured polymer thin films can be fabricated by an oblique angle polymerization method. [1-2] These structures are composed of approximately 40,000,000 aligned columns (approximately 100-150 nm in diameter) per square millimeter similar to the gecko footpad or insect wing. These structures have high aspect ratio and the production technique does not require any template, lithography method or a surfactant for deposition. This approach allows us to tune the chemical properties of nanostructured surfaces and film morphology to control the physicochemical properties of the resulting films, such as hydrophobicity, porosity, electrochemistry, chemical reactivity, surface energy and crystallinity. We have recently functionalized nanostructured polymer films for controlled release and delivery of organics and synthetic molecules. Structured polymer brushes are envisioned to be useful in for specific controlled drug release, metallization (SERS and catalyst applications), tissue targeting as well as antifouling applications. [3-5]

Cetinkaya, M., Malvakdar, N., Demirel, M.C., "Power-Law Scaling of Structured Poly(p-xylylene) Films Deposited by Oblique Angle", JOURNAL OF POLYMER SCIENCE PART B: POLYMER PHYSICS, Vol. 46, pg 640-648, 2008.

Cetinkaya, M., Boduroglu, S., Demirel, M.C. "Growth of Nanostructured Thin Films of Poly(p-xylylene) Derivatives by Vapor Deposition", POLYMER, Vol.48, pg. 4130-4134, 2007

Demirel, M.C., Cetinkaya, M., Singh, A., Dressick W.J., " A Non-Covalent Method for Depositing Nanoporous Metals via Spatially Organized Poly(P-xylylene) Films", ADVANCED MATERIALS, Vol.19, pg.4495-4499, 2007

Boduroglu S., Cetinkaya, M., Dressick, W., Singh, A., **Demirel, M.C.,** "Controlling Wettability and Adhesion of Nanostructured Poly-(p-xylylene) Films", LANGMUIR, Vol.23,pg. 11391-11395, 2007

Kao, P., Malvadkar N., Wang, H. Allara, D., Demirel, M.C., "Surface Enhanced Raman Detection of Bacteria on Metalized Nanostructured Poly(p-xylylene) Films " Vol. 20, pg. 3562-3565, ADVANCED MATERIALS, 2008.

9:40am **TF1+SE-TuM6 Structural and Optical Properties of Metal Sculptured Thin Films on Large-Scale Prepatterned Substrates***, D. Schmidt, T. Hofmann,* ***E. Montgomery***, University of Nebraska-Lincoln*, B. Mbenkum,* Max Planck Institute for Metals Research, Germany*, M. Schubert, E. Schubert*, University of Nebraska-Lincoln

Three-dimensional (3D) metal nanostructures are of particular research interest in modern material science and engineering, due to their intriguing properties, which can differ considerably from their bulk counterparts. These size- and structure-driven properties in such 3D metal nanostructures credit themselves for potential implementation in optical, electro-mechanical, and electromagnetic systems.

We utilize glancing angle physical vapor deposition, which exploits physical shadowing and varying particle incidence azimuth for fabrication of 3D nanostructures from metals arranged in sculptured thin films (STFs). While such nanoscaffolds (typically in geometries of (slanted) columns, chevrons, screws, or spirals) are randomly distributed on untreated substrates, organized growth can be achieved on prepatterned surfaces. Self-assembled block copolymer nanolithography and nanosphere lithography are promising techniques to accomplish wafer-scale prepatterning. The desired spacing of the resulting hexagonal pattern can be tailored based on polymer chain length and nanosphere radius, respectively. Both methods are superior to conventional and electron beam lithography techniques because of small structure sizes achieved in the order of a few nanometers and large scale preparation.

This presentation elucidates our work on structure-related optical properties of different STFs from various metals grown on untreated as well as prepatterned silicon substrates by electron-beam evaporation at an oblique angle of incidence. Generalized spectroscopic ellipsometry is employed to determine the anisotropic optical constants (refractive index n and extinction coefficient k) of the thin films in the spectral range from 400 nm to 1650 nm. All investigated STFs show extreme birefringence as well as dichroism. We observe that optical properties depend rather on geometry than material [1,2].

[1] D. Schmidt, B. Booso, T. Hofmann, A. Sarangan, E. Schubert, and M. Schubert, Appl. Phys. Lett. **94**, 011914 (2009).

[2] D. Schmidt, B. Booso, T. Hofmann, A. Sarangan, E. Schubert, and M. Schubert, Opt. Lett. **34**, 992 (2009).

10:40am **TF1+SE-TuM9 On the Uniformity of Films Fabricated by Glancing Angle Deposition**, ***N.G. Wakefield***, *J.C. Sit*, University of Alberta, Canada

Films fabricated using the glancing angle deposition technique are subject to significant variations in important film parameters across a sample due to varying geometric conditions at each point on the substrate. This is a serious fundamental problem, as non-uniformities in aspects such as film thickness or porosity can drastically change a film's properties across even a small sample size. This means that film properties can vary rapidly, and undesirably, with position over a substrate and attempting to scale technologies based on glancing angle deposition to large areas presents a major challenge. This paper presents a method to quantify the non-uniformities in these quantities, starting from a simple geometric framework, applicable to physical vapor deposition at low pressures. In this work, this method is applied to glancing angle depositions done at a fixed deposition angle, but with arbitrary azimuthal substrate rotation. Quantities such as the effective deposition angle and the mass flux at any point on the substrate can be determined purely from the geometry of the deposition setup. Predicting further quantities such as the film porosity and thickness requires additional, material specific information that is easily obtainable. For a TiO2 deposition at $\alpha = 70°$ on a 10 cm substrate, dependent on the film's structure, porosity and thickness non-uniformities are found to range from ±1.7% to ±8.2% and ±1% to ±30% respectively. Experimental values were obtained using Mueller matrix spectroscopy and showed excellent agreement. The technique described here is general and can be applied to glancing angle deposition setups having arbitrary substrate size and throw distance. The ability to accurately model the gradients in quantities such as the film porosity, allows for a combinatorial approach to examine film properties such as refractive index, absorption or conductivity across a single substrate. Further improvements to the model should allow for the treatment of depositions done at varying deposition angles and with curved substrates.

11:00am **TF1+SE-TuM10 Nanostructured Tungsten and Tungsten Trioxide Films Prepared by Glancing Angle Deposition**, ***D. Deniz***, *R.J. Lad*, University of Maine

The sensitivity of chemiresistive metal oxide gas sensors can be markedly increased by fabricating nanostructured films with very high surface to volume ratio. In this work, nanostructured tungsten (W) and tungsten oxide (WO_3) films were fabricated using pulsed direct current (DC) magnetron sputtering of a W target with a glancing angle deposition (GLAD) geometry. The major parameters that were varied included substrate temperature, deposition rate, substrate rotation, Ar/O_2 plasma composition, and post-deposition thermal treatments. The stoichiometry of the nanostructured films was characterized by X-ray photoelectron spectroscopy (XPS), and the structure and morphology were investigated using X-ray diffraction (XRD) and high resolution scanning electron microscopy (SEM). Metallic W nanorods were formed by sputtering in a pure Ar plasma at room temperature and they crystallized in a simple cubic β-phase with W(100) texture. Subsequent annealing at 500 °C in air transformed the nanorods to textured triclinic WO_3 structure but the nanorod morphology was retained. Stoichiometric WO_3 films grown in Ar/ O_2 plasma at room temperature had an amorphous structure and also exhibited a nanorod morphology. Post-deposition annealing at 500 °C in air induced crystallization to the triclinic WO_3 phase and also caused a morphological change into a very nanoporous network. The differences in the chemiresistive response to each of these high surface area nanoengineered films to CO_2 and CH_4 gas exposure will be presented.

11:20am **TF1+SE-TuM11 Dual Magnetron Oblique Sputtering of Biaxially Oriented ZnO Thin Films on Amorphous Substrates**, ***B.L. Stevens***, *S.A. Barnett*, Northwestern University

This talk will describe results on deposition and characterization of biaxially oriented ZnO thin films on amorphous substrates. Biaxially-oriented ZnO thin films on low-cost substrates are of interest for ZnO-based devices and as “substrates” for subsequent growth of devices based on AlN, GaN, InN, and their alloys. Expensive single crystal substrates, which are typically used to achieve the requisite crystalline perfection of the epitaxial device layers, could be replaced by biaxially-textured ZnO substrates if sufficiently good orientation can be achieved.

The dual magnetron oblique sputtering (DMOS) geometry utilized two dc magnetron sputter sources, with metallic Zn targets, positioned opposite each other and at angles of 20 to 40^o relative to the substrate normal. Sputtering was carried out in an oxygen-rich Ar-O_2 atmosphere. Substrates were Corning 7059 glass, Corning 1737F glass, or Si (001) that had been oxidized to produce an amorphous SiO_2 surface layer. Cross-sectional SEM showed reasonably dense as-deposited films even without substrate heating. The as-deposited films were under considerable compressive stress, as measured by x-ray peak position, in agreement with prior results on sputtered ZnO. Atomic-force microscopy measurements on as-deposited 1.5 µm thick films showed relatively high rms roughnesses of 8.3 nm.

The ZnO films exhibited (002) out-of-plane orientation, as suggested by θ-2θ x-ray scans and verified by x-ray pole figures that were completed for selected samples. Sputtering from a single target (instead of the usual dual-target geometry) caused a shift in the out-of-plane orientation, causing the (002) plane normal to be up to 10° off normal. X-ray scans as a function of azimuthal angle Φ were carried out to detect reflections from (101) planes. The strongest biaxial orientation was observed when the sputter sources were placed at 30^o from the substrate normal, with Φ-scan peaks exhibiting a full width half maximum (FWHM) value of 23°. Elevated substrate temperature during deposition, up to 600°C, decreased the orientation in the films, yielding a ~17% increase in Φ FWHM. Post deposition annealing at up to 1000°C substantially improved the degree of biaxial orientation, decreasing the Φ-scan FWHM by ~60%. The effects of a range of deposition and post-deposition annealing conditions on the film orientation will also be reported. The orientation mechanism also will be discussed.

11:40am **TF1+SE-TuM12 A Slice of GLAD: Use of Focused Ion Beam Tomography to Characterize Titania Thin Films**, ***K.M. Krause***, University of Alberta, Canada, *D. Vick*, NRC National Institute for Nanotechnology, Canada, *M.J. Brett*, University of Alberta, Canada

Focused ion beam (FIB) tomography allows for the serial slicing and imaging of a sample volume on the order of several nanometers to microns thick. With this technique, a focused beam of ions rasters across the specimen surface, milling it layer-by-layer. In tandem, a scanning electron microscope (SEM) images the exposed surface at the removal of each individual slice. The series of SEM images can then be post-processed with custom or commercially available software to create a 3D reconstruction of the milled volume.

As FIB tomography has progressed over the years, the range of materials, structures, and size scales has been expanded. Various analysis have been carried out with FIB, including the study of how grain boundaries in Ni alloys influence crack propagation and how the geometry of buried Ge quantum dot superlatices depends on the growth of supporting materials layers [1 – 3]. In the present work we report on the use of ion beam milling and concurrent SEM imaging to probe the properties of titanium dioxide nanostructured thin films fabricated using the glancing angle deposition (GLAD) technique [4].

Our titania films are deposited at oblique angles, while substrate rotation is employed, on silicon wafers. The resultant films have a columnar structure with spacing between columns determined by the deposition angle and characteristics determined by the rotation speed and deposition rate. To support the porous GLAD films during FIB slicing, a photoresist is spun into the film and then baked, forming a heterogeneous solid. The photoresist not only provides support for the nanostructures as they are sliced, but also offers good atomic number (Z) contrast to the titania. The GLAD films are then sliced and imaged using a Zeiss NVision 40 Crossbeam® workstation. Captured images are post-processed using MATLABTM and commercially available JEOL TEMographyTM software packages.

While column morphology and geometric properties of GLAD films have been well studied, investigations of columnar structure have been limited to SEM and TEM. Here, we demonstrate that the FIB technique can be used to provide a spatially discrete view of GLAD intra-column and inner-column porosity and structure. Analysis of these properties is ongoing and current experimental results will be presented.

References

1. C. Holzpfel, W. Schaf, M. Marx, H. Vehoff, F. Mucklich, Scripta Materialia 56, 697-700 (2007).

2. E. Keehan, L. Karlsson, H.K.D.H Bhadeshia, M. Thuvancer, Materials Characterization 59, 877-882 (2008).

3. A.H. Kubis, T.E. Vandervelde, J.C. Bean, D.N. Dunn, R. Hull, Applied Physics Letters 88, 263103 (2006).

4. K. Robbie, M.J. Brett, A. Lakhtakia, Nature 384, 616 (1996).

Thin Film
Room: B4 - Session TF2-TuM

ALD/CVD: Basics, Organics, Electronics
Moderator: R.G. Gordon, Harvard University

8:00am **TF2-TuM1 How Surface Reactions Afford Ultra-Conformal CVD: A Zone Diagram and the Application of Suppressor Species**, ***J.R. Abelson***, University of Illinois at Urbana-Champaign **INVITED**

We present a unified description of conformal film growth in recessed features by low-pressure chemical vapor deposition. Experimental data on step coverage and growth rate are interpreted in terms of a Langmuirian kinetic model for the elementary surface processes. This model is combined with the continuity equation for gas transport and consumption to predict the values of precursor pressure and substrate temperature (p,T) that are necessary for conformal coverage to occur for a given precursor. We introduce a *conformal zone diagram* that considers the gas phase limitations (maximum precursor pressure, onset of secondary reactions), the surface limitations (minimum reaction temperature, precursor adsorption and desorption rates, film growth rate) and the aspect ratio of the feature to be coated; the allowed intersection between the resulting boundaries defines the (p,T) zone for conformal growth. Sufficient precursor pressure is identified as a major requirement for conformal film growth, one that is not met by many commercially available molecules. We show that *growth inhibition*, the use of a second species to decrease the surface reactivity, can enlarge the conformal zone of low-pressure precursors. We incorporate the inhibition mechanism into the kinetic model; the theoretical predictions are in excellent agreement with experimental results. We also extend the kinetic model to the case of compound film growth from two reactants. Finally, we derive an approximate analytical solution to the inverse problem: what are the experimental conditions necessary to afford a desired degree of step coverage on a given aspect ratio feature at a desired growth rate. The solution depends on a set of rate constants in the kinetic model that can be extracted from measurements of the film growth rate as a function of precursor pressure and substrate temperature on trench or planar substrates.

8:40am **TF2-TuM3 Functional and Conducting Polymer Thin Films by Vapor Deposition**, ***K. Gleason***, Massachusetts Institute of Technology **INVITED**

Polymers provide extraordinary opportunities for functionalizing surfaces and creating thin films for integration into flexible devices. Vapor deposition is the method of choice for polymers having limited solubility or if the object to be coated degrades or swells upon exposure to solvent. Indeed, fluoropolymers, cross-linked materials, and electrically conducting polymers are three examples of organic materials which having little if any solubility, but which have been successful deposited by two new vapor phase methods: initiated chemical vapor deposition (iCVD) and oxidative chemical vapor deposition (oCVD). By depositing polymers from the vapor phase, many wetting and solution effects are avoided, and conformal films can be created. The iCVD method is a platform technology which has produced more than 40 different homopolymers. Random copolymers, alternating copolymers, and grafted polymer chains have all been demonstrated using the iCVD method. Surface properties achieved include non-leaching antimicrobial layers, flexible dielectrics with low leakage current, and coatings with specific ligand binding capability on porous substrates and particles, superhydrophobicity, and superhydrophilicity. Engineering of iCVD coatings has led to extremely stable and flexible biopassivation coatings for neural implants, reversible swellable hydrogel layers, and enteric coatings of drug particles for pH sensitive release. Mechanistic understanding of the oCVD growth mechanism led to the ability to propagate conductive polymer chains directly from the growth surface with the use of any additional linker molecules. The creation of durable covalent linkages between the substrate and the surface functionalization layer affords excellent adhesion and also enables 60 nm lithographic pattern formation. The demonstration of patterns in conducting polymer patterns grafted onto common plastic substrates is a potential breakthrough for integrated circuitry for flexible electronics where mechanical robustness is extremely important, requiring excellent interfacial properties and adhesion. Each organic thin film synthesized by iCVD and oCVD displays a well-defined chemical structure as a result of selectively limiting the reaction pathways available during processing through a judicious choice of reactants and minimizing the energy input that drives the CVD chemistry. The exquisite control over composition and conformality achieved by these new vapor phase methods enables precise organic functionality to be designed and applied to almost any type of substrate. The fundamental understanding of the processes accelerates both discovery of and scale-up.

9:20am **TF2-TuM5 CVD of Three Aminosilanes on Silicon Oxide: Effect of Silane Concentration, Surface Characterization and Stability, and Cyanine Dye Adsorption**, ***M.R. Linford***, *F. Zhang,* Brigham Young University*, H. Samha,* Southern Utah University*, K. Sautter,* Yield Engineering Systems*, R.C. Davis*, Brigham Young University

Amino silanes are among the most frequently deposited reagents for surface modification to prepare biosensors and other biologically active materials. Of the various ways to deposit silanes, it is becoming increasingly recognized that CVD is the most reproducible and reliable. However, CVD of these important reagents is also much less studied than the less reproducible and much more widely practiced deposition from solution. We also stress the environmentally friendly and industrially viable nature of CVD silane deposition. Our work differs from that of most academic researchers because of the tool we use for silane deposition, which is a commercially available CVD system (the 1224P) from Yield Engineering Systems. This tool gives complete control of oven temperature, pressure, and reagent delivery, in addition to offering plasma pretreatment of the substrates at a range of powers and conditions. In our work we have explored the CVD at 150°C of 3-aminopropyltriethoxysilane (APTES), which is arguably the most widely used and important silane. We show that surface saturation leading to the same level of surface functionalization occurs over a very wide range of gas phase concentrations. This important result indicates that there is a wide process window for APTES deposition. We further compare CVD of APTES to the gas phase deposition of two of its aminosilane analogs – one with two methyl groups (3-aminopropyldimethylethoxysilane), and the other with two isopropyl groups (3-aminopropyldiisopropylethoxysilane). X-ray photoelectron spectroscopy (XPS) shows a decrease in nitrogen concentration for these two molecules compared to APTES. All of these films are extremely flat by atomic force microscopy, and spectroscopic ellipsometry indicates the expected monolayer coverages of our silanes. Of particular significance is the stability against base of the diisopropyl aminosilane, which should make it valuable in a number of applications. The interactions of our different amino surfaces with a cyanine dye are also probed, and the structure/adsorption of the dye seems to be well correlated to the amine density determined by XPS.

9:40am **TF2-TuM6 Novel Precursors for CVD of Amorphous and Crystalline Cobalt Group Metal-Phosphide Films***, **J. Rivers**, R. Jones*, The University of Texas at Austin

Volatile Cobalt group complexes were synthesized as single-source precursors for chemical vapor deposition of amorphous and crystalline metal-phosphide thin films. Phosphide alloys of transition metals are of interest due to their use as barriers against corrosion, electrodes, batteries, catalysts, and as diffusion barrier layers in integrated circuits. Volatile precursors allow use of CVD which is advantageous to other physical methods such as PVD. Precursors were specifically designed and synthesized utilizing ligands which impart volatility such as 3,5-bis(trifluoromethyl)pyrazole and trimethylphosphine. Complexes studied include $[Rh((CF_3)_2\text{-}Pz)(PMe_3)_3]$, $[Co(PMe_3)_4]$, $[Co((CF_3)_2\text{-}Pz)\ (PMe_3)_3]$, and $[Co((CF_3)_2\text{-}Pz)_3(PMe_3)][CoH(PMe_3)_4]$. The nature of the films depends on reactor conditions such as flow rate, deposition time, substrate temperature, and annealing conditions. Films were grown at temperatures under 400 ^oC in a hot-wall reactor utilizing dynamic vacuum or Ar as a carrier gas and characterized using XPS, XRD, and SEM.

10:40am **TF2-TuM9 Kinetic Study on InGaAsP-MOCVD Using Selective Area Growth and its Application to OEIC Device Fabrication***,* ***Y. Shimogaki***, The University of Tokyo, Japan **INVITED**

Metal-organic chemical vapor deposition (MOCVD) is a well developed deposition technology for the fabrication of InGaAsP compound semiconductors. If the substrate is partially covered by dielectric masks such as SiO_2, selective growth will occur and no growth takes place on the mask during the MOCVD. Then reactants will be accumulated above the mask area and migrate towards the adjacent non-mask covered area, causing growth rate enhancement. This growth rate enhancement will be proportional to the size of the mask, because larger mask will accumulate more reactants. Thus we can control the selective growth rate by the area of the mask. This technique is called selective area growth (SAG). The thickness, composition, and even the properties of the SAG-epitaxial layers can be locally tailored by specifically designed mask patterns. For example, in the single-step growth of multiple-quantum-well structures (MQWs) on well-designed mask patterns, it is possible to control the effective band gap energy of the layers by changing the well width and composition. Thus, passive and active devices can be locally integrated simultaneously by designing the mask size and pattern. This technology will reduce the cost of fabrication and enhances production yield of opto-electronic integrated circuit (OEIC).

Numerical simulation on growth rate non-uniformity of SAG in sub-millimeter scale can extract real surface kinetics in MOCVD process for InGaAsP-compounds, which is normally hindered by mass transport rate of film precursors [1]. SAG analysis with non-linear surface kinetics is introduced for the first time to analyze group-III precursor partial pressure dependency of InGaAsP-MOCVD [2]. Important kinetic parameters, such as surface reaction rate constant, adsorption equilibrium constant, and surface coverage, have been extracted. Such non-linear kinetic analysis using SAG (micro analysis) is combined with computational fluid dynamics (CFD) reactor-scale analysis (macro analysis) to elucidate the main reaction mechanism of InGaAsP-MOCVD process in the whole reactor. The design of photo-luminescence (PL) wave length for optical device by tailoring the mask pattern will be demonstrated.

References

1. H.J. Oh, M. Sugiyama, Y. Nakano, and Y. Shimogaki, *Jpn. J. Appl. Phys.*, **42** (2003) 6284.

2. Y. Wang, H. Song, M. Sugiyama, Y. Nakano, and Y. Shimogaki, *Jpn. J. Appl. Phys.*, **48** (2009) 041102.

11:20am **TF2-TuM11 OLED Encapsulation by Room Temperature Plasma-Assisted ALD Al_2O_3 Films**, ***W. Keuning***, *M. Creatore, E. Langereis,* Eindhoven University of Technology, Netherlands*, H. Lifka, P. van de Weijer,* Philips Research Laboratories, Netherlands*, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Organic light emitting diodes (OLEDs, both small molecule and polymer LEDs) require excellent gas and moisture permeation barrier layers to increase their lifetime. The quality of the barrier layer is ultimately controlled by the presence of defects in the layer. Although a barrier layer may be intrinsically excellent (water vapor transmission rate, WVTR $\leq 10^{-6}$ $g{\cdot}m^{-2}{\cdot}day^{-1}$) the protected device may fail in the presence of defects that lead to preferential diffusion pathways for H_2O (e.g., defects caused by particles from the environment and/or production process). The state-of-the-art barrier coatings are micrometer-thick multi-layer structure, in which organic interlayers are alternated with inorganic barrier layers with the purpose of decoupling the above-mentioned defects. Recently, atomic layer deposition (ALD) has been successfully tested for the deposition of very thin (< 50 nm) single layer permeation barriers on pristine polymer substrates [1,2], showing the potential of this highly uniform and conformal deposition technique in the field of moisture permeation barriers. In this contribution the encapsulation of OLEDs by plasma-assisted ALD of thin (20-40 nm) Al_2O_3 layers is addressed. The layers are synthesized at room temperature by sequentially exposing the substrate to $Al(CH_3)_3$ vapor and a remote inductively coupled O_2 plasma in Oxford Instruments FlexAL^{TM} and OpAL^{TM} reactors. The intrinsic quality of the deposited ALD layers was determined by monitoring the oxidation of a Ca film encapsulated by the Al_2O_3 film: WVTR values as low as $2\cdot10^{-6}$ $g\cdot m^{-2}\cdot day^{-1}$ have been measured. The potential of ALD layers in encapsulating OLEDs, and therefore in successfully covering the defects present on the device, has been investigated by means of electroluminescence measurements of polymer-LEDs (effective emitting area of 5.8 cm^2). The black spot density and area growth were followed as a function of the time under standard conditions of 20°C and 50% relative humidity. Within a 500 h test ALD-encapsulated OLEDs show approximately half the black spot density compared to devices encapsulated by plasma deposited a-SiN_x:H (300 nm thick). The black spot density is further reduced by combining the a-SiN_x:H and ALD Al_2O_3 layers. These results point towards a very promising application of ALD Al_2O_3 layers in the field of OLED encapsulation and will be interpreted in terms of possible mechanisms related to film growth in multi-layer structures.

---

[1] M.D. Groner, S.M. George, R.S. McLean, P.F. Carcia, Appl. Phys. Lett. **88**, 051907 (2006)

[2] E. Langereis, M. Creatore, S.B.S. Heil, M.C.M. van de Sanden, W.M.M. Kessels, Appl. Phys. Lett. **89**, 081915 (2006)

11:40am **TF2-TuM12 Controlled Doping of CVD Diamond with Mid-to-High Z Metals**, ***M.M. Biener***, *J. Biener,* Lawrence Livermore National Laboratory, *H. Obloh,* Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *S.O. Kucheyev, Y.M. Wang,* Lawrence Livermore National Laboratory, *W. Mueller-Sebert,* Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *B.S. El-Dasher,* Lawrence Livermore National Laboratory, *A. Kriele,* Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *N.E. Teslich Jr.,* Lawrence Livermore National Laboratory, *C. Wild,* Fraunhofer-Institut für Angewandte Festkörperphysik, Germany, *A.V. Hamza*, Lawrence Livermore National Laboratory

The development of diamond chemical vapor deposition (CVD) techniques has led to numerous thin film applications. Besides grain boundary engineering, doping is one way to further optimize diamond's unique materials properties for a given application. Here, we report on controlled doping of synthetic diamond with Mo and W by adding volatile metal precursors to the diamond CVD growth process. Effects of deposition temperature, grain structure and precursor exposure on the doping level are systematically studied. The metal atoms are uniformly distributed throughout the CVD diamond film, and doping levels of up to 0.25 at.% have been achieved. Rutherford backscattering/ channeling experiments reveal that the metal atoms do not occupy substitutional or interstitial sites, thus suggesting the formation of more complex sites such as metal-vacancy clusters.

Work at LLNL was performed under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344.

Exhibitor Workshops
Room: Exhibit Hall 1 - Session EW-TuL

Exhibitor Workshop
Moderator: B.R. Rogers, Vanderbilt University

12:40pm **EW-TuL3 New Developments in Spectroscopic Imaging from Thermo Fisher Scientific**, ***R.G. White***, *A.E. Wright, J. Wolstenholme*, Thermo Fisher Scientific, UK

Surface structure and chemistry are crucial to the successful production and operation of innumerable devices, materials and coatings. X-ray photoelectron spectroscopy, with its high surface specificity and chemical state sensitivity, is an ideal tool for the evaluation of material composition. XPS spectroscopic imaging, in which spectral data are acquired with some degree of lateral resolution, allows the identification of both spatial and chemical variations in materials. The expansive data sets that result from spectroscopic imaging must be treated with powerful software algorithms, to extract high levels of spatial and chemical information with a minimum of acquisition time.

Spectroscopic imaging solutions to structural and chemical problems are presented using the full range of state-of-the-art fully integrated X-ray Photoelectron Spectrometers from Thermo Fisher Scientific. Such analyses demonstrate the importance of small-scale structure on the integrity of a polymer blend, show the consequences of corrosion/dissolution of metallic and polymeric surfaces, and illustrate the nature of bonding failures. The effectiveness of spectroscopic imaging analyses, and intensive, automated data refinement processes using award-winning Avantage datasystem, are shown for each of these examples.

1:00pm **EW-TuL4 State-of-the-Art Nanostructure Compositional Analysis with Scanning Auger Microscopy**, ***J.S. Hammond***, *D.F. Paul, J.F. Moulder*, Physical Electronics

Advances in nanotechnology research now require analytical techniques that can image the elemental and chemical compositions of novel three dimensional structures. To meet these needs, a new state-of-the art Scanning Auger Nanoprobe has been developed with high energy resolution chemical state spectroscopy combined with Auger imaging uniquely tailored to nanostructure morphologies. The instrument design will be briefly discussed and highlights from the analysis of several nanostructures structures will be reviewed.

1:20pm **EW-TuL5 State of the Art in XPS**, *C.J. Blomfield,* Kratos Analytical Ltd, UK, ***D.J. Surman***, Kratos Analytical

Modern XPS instruments such as the Axis range from Kratos Analytical offer a variety of analytical capabilities extending beyond simple chemical characterisation of the upmost layers of a material surface. Advances in ion gun technology, chemical imaging resolution, instrument spectroscopic performance and data processing have made analysis faster, data more accurate and the previously impossible possible. XPS is becoming more wide spread with new users from fields such as photovoltaics, biocompatibility, pharmaceuticals and nano-science enjoying the benefits of surface analysis.

More specifically; improvements in ion gun technology have meant low energy monatomic sources can give better interface quality for multi-layer inorganic materials. The development of polyatomic ion sources has made XPS depth profiling of organic materials feasible. XPS imaging has developed into a technique to quantitatively characterise surface inhomogeneity and the application of multivariate data analysis techniques has reduced acquisition times while improving information content. Angle resolved XPS has benefited from new interpretation routines via the application of maximum entropy analysis methods to extract meaningful, non destructive, concentration profiles over the first few nanometres.

This presentation aspires to give an overview of the state of the art in XPS driven surface analysis by presenting examples and case studies from a number of important application areas ranging from thin film photovoltaics to bio-compatibility. Examples where hardware and software advances have helped the analyst will be given for techniques such as auto quantification, XPS depth profiling, angle resolved XPS, chemical state imaging, work function determination and electronic structure characterisation.

Applied Surface Science
Room: C2 - Session AS+NS-TuA

Nanoparticle and Nanoscale Surface Chemistry I
Moderator: V. Grassian, University of Iowa

2:00pm **AS+NS-TuA1 Hydrogen Interactions on Nanostructured Carbon Aerogel Surfaces**, ***T.M. Willey,*** Lawrence Livermore National Laboratory, *A. Deriy,* Argonne National Laboratory, *B.J. Kozioziemski, M. Worsely, G. Nyce, J.R.I. Lee,* Lawrence Livermore National Laboratory, *J. Ilavsky,* Argonne National Laboratory, *S. Ghosal, K.J. Wu, A.V. Hamza, T. van Buuren*, Lawrence Livermore National Laboratory

Generating clean power from nuclear fusion has been an elusive goal over the past several decades. Although many incremental improvements continue towards this goal, one of several challenges for inertial confinement fusion (ICF) is to produce inexpensive, highly symmetric and/or highly controlled deuterium-tritium ice layers within millimeter-sized spherical targets. Ultra low density, nanostructured materials such as aerogels could be useful to serve as scaffoldings for forming uniform hydrogen ice layers. We have studied the aerogel structure and as well as nanoscale wetting of liquid hydrogen onto aerogel surfaces using ultra small angle x-ray scattering (USAXS). We have focused on two 30 mg/cc carbon aerogel structures; the first is a dicyclopentadiene (DCPD) polymer aerogel and the second, a carbon nanotube based aerogel. We are able to observe and control nanoscale hydrogen droplet formation within the DCPD structure, while scattering from nanotube-based aerogels indicates wetting with little or no indication of droplet formation. The combination of ultra-low density, hydrogen uptake, and wetting differences are promising developments for materials to be used in designer targets for ICF. Both aerogels, but especially the nanotube-based aerogel exhibit minimal structural changes when submerged and frozen in cryogenic hydrogen.

2:20pm **AS+NS-TuA2 Probing the Surface Chemistry and Catalytic Activity of Bimetallic and Oxide Nanoparticles**, ***L. Jones***, *M. Gordon*, University of California Santa Barbara

Catalysis by metallic nanoparticles offers a wide variety of model systems to study and understand the fundamental mechanisms involved in surface chemistry. In addition, dramatic changes in catalytic activity have been observed when transitioning from the bulk phase to nanoscale dimensions. This behavior is mainly due to finite size effects (i.e., unsaturated atoms at surfaces, edges, kinks, and corners), preferred morphologies, or modification of the nanoparticle’s electronic structure by the support. Being able to observe these changes as nanoparticles are decreased in size can give more insight into how to tune electronic and structural changes for particular catalytic applications.

In this talk, we will highlight several routes to synthesize monodisperse metallic nanoparticles (Cu, Pt, Au) of sizes <10 nm with different shapes and compositions. We will also discuss the formation of ordered arrays of supported metallic nanoparticles via plasma reduction of micelles containing metallic precursors. The talk will include catalytic studies, in-situ vibrational spectroscopy, and XPS on Cu and its oxides for CO oxidation as a function of particle size, support, and promoters. The Cu/Cu2O/CuO system has been studied using controlled oxidation and CO/O2 dosing at various temperatures and pressures, using Raman bands of adsorbates and phonons to investigate changes in catalytic mechanisms, activity, and nanoparticle morphology.

2:40pm **AS+NS-TuA3 STXM Spectroscopy of Individual Polymer-Wrapped Carbon Nanotube**, ***J.J. Pireaux***, *X. Gillon, S. Abou Rich, A. Felten*, University of Namur (FUNDP), Belgium

The intrinsically inert nature of the pristine carbon nanotube (CNT) surface is a severe constraint for several applications such as fabrication of composites in which the CNTs should be homogeneously dispersed in a matrix. To overcome this problem, functionalisation of the CNT surface has been attempted with different methods (chemical or electrochemical modification, polymer grafting, fluorination…). Our most recent approach consists in the use of Inductive RF plasma (13.56 MHz) to polymerize a monomer (acrylic acid or styrene) onto the CNT surface. But when characterizing the composition of such a nano-material with a conventional technique like X-ray Photoelectron Spectroscopy, one faces the problem that typically a sample area of some μm^2 or even mm^2 is probed: this prevents the analysis of an individual modified nanostructure . Moreover, signal originating from impurities present on the nanotube (amorphous carbon, onion-like particles, catalysts residues) cannot be avoided. Clearly, one would like to be capable to carry out the analysis at much higher spatial resolution. In this context, Scanning Transmission X-ray Microscopy (STXM) has recently been shown to be one of the most appropriate techniques to study carbon nanotubes since it combines both spectroscopy and microscopy with a spatial resolution better than 30 nm: STXM allows indeed to study isolated nanotubes [1,2,3]. In this report, electronic, structural and chemical properties of pristine and plasma treated isolated multiwall carbon nanotubes were studied with STXM at beamline 5.3.2. from the Advanced Light Source (ALS), Berkeley (CA). Analysis of the C1s near-edge absorption fine structure (NEXAFS) was performed showing clear differences between grafted polystyrene, polyacrylic acid and the carbon nanotubes. Chemical mapping at the nanoscale was performed, highlighting polymer rich regions on the nanotubes.

This work is financially supported by the Nano2Hybrids project (EC-STREP-033311) and the RCO Marshall plan.

1. A. Felten et al. Appl. Phys. Lett. 89, 093123(2006).
2. A. Felten et al. Nano Lett., 7, 2435(2007).
3. E. Najafi et al. Small, 4 (12), 2279 (2008).

3:00pm **AS+NS-TuA4 Nanoparticle Characterization using Advanced FESEM/STEM and XPS Instrumentation**, ***K.L. Bunker***, *T. Lersch, J. Marquis, Jr., G. Casuccio, J.D. Piasecki, B.R. Strohmeier*, RJ Lee Group, Inc.

Transmission electron microscopy (TEM) and field emission scanning electron microscopy (FESEM) are valuable tools for characterizing the structure, morphology, and composition of nanoparticles and nanostructures. TEM can provide high-resolution imaging, crystallographic information, and elemental composition, when combined with energy dispersive X-ray spectroscopy (EDS), but no detailed surface information. FESEM on the other hand, can provide extremely detailed information on surface morphology. Combining the high resolution secondary electron imaging capabilities of FESEM with TEM data to utilize the strengths of each technology provides the opportunity to more fully and accurately characterize nanomaterials. However, the process of transferring samples between separate FESEM and TEM instruments and relocating such small particles is time consuming and tedious. Recently, Hitachi commercialized a high resolution electron microscope that combines the benefits of FESEM and low-kV scanning transmission electron microscopy (STEM) in a single instrument (Model S-5500).

The electron optical design of the S-5500 places the sample at the optimum analytical and imaging working distance. This allows simultaneous acquisition of high-resolution FESEM and STEM images, as well as EDS information. Therefore, a variety of signals can be collected simultaneously including secondary electron and backscattered electron FESEM images and bright field (BF) and dark field (DF) STEM images. Combining this instrument with new silicon drift detector (SDD) technology (Bruker 30 mm^2) allows for high resolution elemental analysis and mapping of nanostructures.

X-ray Photoelectron Spectroscopy (XPS), also known as Electron Spectroscopy for Chemical Analysis (ESCA), is a highly surface-sensitive and quantitative technique for nanostructured materials characterization. Nanometer scale sampling depth and its ability to provide chemical state information makes XPS an ideal analytical technique for investigating the elemental and chemical composition of nanoparticles. Hence, XPS can provide valuable complementary information to high resolution electron microscopy studies of nanomaterials. This presentation will illustrate the power of using combined FESEM/STEM and XPS analysis through an examination of a variety of nanomaterials. Examples will include (among others): functional thin organic layers on metal surfaces, multi-layer thin film coatings on glass, activated carbon nanoparticles, antimicrobial metal nanoparticles, and carbon nanotubes containing nanoparticle metal catalysts.

4:00pm **AS+NS-TuA7 Behavior of Engineered Nanoparticles in Aquatic Environments – An Overview**, ***R.D. Holbrook***, National Institute of Standards and Technology **INVITED**

The behavior of engineered nanoparticles in aquatic systems will be influenced by three main factors: the physiochemical conditions encountered in a specific environment; the nanoparticles' bioavailability; and any transformation that may occur during biological uptake and excretion. Physiological conditions, such as the type and concentration of organic matter and inorganic species, will dictate aggregation kinetics. Environments that encourage nanoparticle stability may increase their persistence in the water column while those that favor instability may result in nanoparticle deposition among bottom sediments. Nanoparticle bioavailability will be dictated by both spatial and phase distribution; large nanoparticle aggregates bound to sediment material may be less available to aquatic organisms than, for example, single nanoparticles remaining in solution. Biological ingestion and subsequent excretion may result in nanoparticle degradation and/or changes to aggregation behavior. The objective of this presentation is to provide an overview of these three factors as they apply to the fate, transport, and bioavailability of engineered nanoparticles. Information gained from studying naturally-formed nanoparticles (colloids) will be reviewed and case studies will illustrate our current knowledge of engineered nanoparticle behavior.

4:40pm **AS+NS-TuA9 Heads *and* Tails: Simultaneous Exposed and Buried Interface Imaging of Self-Assembled Monolayers**, ***P.X. Han***, *A.R. Kurland,* The Pennsylvania State University*, S.U. Nanayakkara,* University of Pennsylvania*, M. Blake, C.M. Pochas, P.S. Weiss*, The Pennsylvania State University

We have simultaneously imaged the chemically bound head-groups and exposed tail-groups in bi-component alkanethiolate self-assembled monolayers with molecular resolution. This has enabled us to resolve the controversy of scanning tunneling microscopy image interpretation, and to measure the molecular polar tilt and azimuthal angles. Our local measurements demonstrate that ordered domains with different superstructures also have varied buried sulfur head-group structures.

Biomaterial Interfaces
Room: K - Session BI-TuA

Biofouling
Moderator: G.P. Lopez, University of New Mexico

2:00pm **BI-TuA1 Anti-Fouling Hydrogels for Biomaterials and Sensing Applications**, ***B.G. Liedberg***, Linköping University, Sweden **INVITED**

The present contribution describes a novel set of hydrogel coatings prepared by self-initiated photografting and photopolymerization (SIPGP). The method is based on UV free radical polymerization of methacrylate and acrylate monomers into 0-200 nm thick coatings on top of virtually any organic/polymeric substrate. The vast majority of the coatings are based on different mixtures of PEG containing methacrylates. These hydrogels display excellent protein rejecting properties in simple single component solutions and mixtures, as well as in serum and plasma [1]. Recent studies on platelet adsorption looks also were promising. The UV fabrication technology is also compatible with patterning on the micrometer length scale, thus providing an attractive platform for biochip development and microarraying [2]. The preparation of gradients is also discussed for tuning the physio/chemical properties of the hydrogel coatings [3]. A novel set of charged balanced hydrogel gradients have been prepared for studies of protein adsorption from protein mixtures and plasma with encouraging results [4]. Finally we describe an approach for array fabrication of nanobrushes/bushes on a pre-patterned template generated by Dip Pen Nanolithography (DPN).

1. A. Larsson, T. Ekblad, O. Andersson, B. Liedberg, *Biomacromolecules*, **8**, 287-295 (2007).
2. A. Larsson, C-.X. Du, B. Liedberg, *Biomacromolecules*, **8**, 3511 (2007).
3. A. Larsson, B. Liedberg, *Langmuir*, **23**, 11319 (2007).
4. T. Ekblad, O. Andersson, F.-I. Tai, T. Ederth, B. Liedberg. *Langmuir*, **25**, 3755 (2009).

2:40pm **BI-TuA3 Emerging Strategies to Prevent Bacterial Colonization of Medical Biomaterials**, ***J.D. Bryers***, University of Washington **INVITED**

Nosocomial (hospital-acquired) infections are the fourth leading cause of death in the U.S. with >2 million cases annually (or ~10% of American hospital patients). About 60-70% of all such infections are associated with an implanted medical device causing >$4.5 billion medical costs in 2002 and ~99,000 deaths annually. Over 65% of hospital-acquired infections are associated with implants or indwelling medical devices, with the case-to-fatality ratio between 5-50%. It is estimated that over 5 million artificial or prosthetic devices are implanted per annum in the U.S. alone. Microbial infections have been observed on most biomedical devices, including: prosthetic heart valves, orthopedic implants, intravascular catheters, artificial hearts, left ventricular assist devices, cardiac pacemakers, vascular prostheses, cerebrospinal fluid shunts, urinary catheters, ocular prostheses and contact lenses, and intrauterine contraceptive devices.

Traditional strategies to control medical device-based biofilm infections are based on the use of compounds that kill or inhibit the growth of *freely suspended* bacteria. However, "biofilm-bound" bacteria tend to be significantly less responsive to antibiotics and antimicrobial stressors than planktonic organisms of the same species. In fact, studies have shown that sub-lethal doses of antibiotics can exacerbate biofilm formation. Consequently, systemic antibiotic treatment typically fails to clear a biofilm infection and inevitably requires removal of the device. Moreover, the risk of antibiotic resistance development is drastically increased under the current standard use of systemic antibiotic treatment of medical-device infections.

Here novel non-antibiotic based concepts in biomaterials design (novel stealth surfaces or biomaterials that biologically prevent bacterial colonization) will be presented.

4:00pm **BI-TuA7 Protein Adsorption - Influence from Surface and Protein Characteristics**, ***M. Holmberg***, *X. Hou*, Technical University of Denmark

Competitive protein adsorption from human serum and protein mixtures onto unmodified and plasma polymerised polymer surfaces has been investigated using radioactive multi-labelling. By using several different isotopes it is possible to monitor several proteins simultaneously and thereby analyse the interaction between the different proteins during adsorption processes.

The outcome of competitive protein adsorption depends on both surface and protein characteristics, as well as parameters such as protein concentration and adsorption sequence. In this study surface characteristics of polymer surfaces have been modified by using plasma polymerisation where the polymer surface becomes more hydrophilic. Modified surfaces show non-fouling characteristics and have shown to be stable in buffer solutions for at least 24 hours. By changing the sequence of proteins introduced to a surface, different outcome from an adsorption series with the same proteins can be observed and by changing the internal ratio between different proteins concentration, different proteins will dominate the surface during adsorption.

Even though some polymer surfaces show protein monolayer adsorption behaviour and quite low amount of proteins adsorbed, other surfaces loose there resistance to protein adsorption as the protein concentration increases, and on hydrophobic polymer surface one can even see a very thick and cross linked protein multilayer formed. The tendency for protein multilayer formation is also influenced by other proteins present during adsorption and protein characteristics, where some proteins seem to be more fragile during adsorption to hydrophobic polymer surfaces than others.

The objective of the study is two-fold; to investigate basic processes and concepts during competitive protein adsorption and to contribute to development of polymer based biomaterials for use in contact with whole blood.

4:20pm **BI-TuA8 Influence of Physicochemical Surface Properties on the Adhesion of Marine Microorganisms**, ***A. Rosenhahn***, *S. Schilp, X. Cao, F. Wode, M.P. Arpa Sancet, M. Heydt, M. Grunze*, University of Heidelberg, Germany

The prevention of biofouling is a major challenge for all manmade objects which are in long term contact with seawater. In order to systematically develop non toxic coatings, a fundamental understanding of basic surface properties relevant for adhesion of marine inhabitants is required. To determine the influence of selected surface properties we systematically vary wetting, hydration and charge by self assembly of oligo- and polymers. To obtain well defined morphologies, nanolithography and multilayer assembly are used. The biological response is determined in settlement and adhesion strength assays using predominantly the green algae Ulva linza, but also barnacle cyprids and marine bacteria. It turned out that contact angles around the Berg limit, hydration of the coatings and micrometer sized structures render surfaces less attractive. Besides static assays we are interested in the time dependent dynamics of biofilm formation. To acquire and analyze the complex, 3D swimming and exploration patterns of algal zoospores, we apply digital in-line laser holography. The influence of surface properties on the motion patterns and surface recognition will be discussed.

4:40pm **BI-TuA9 *In situ* Characterization of Barnacle Primary Cement Interfaces by ATR-FTIR Spectroscopy**, ***D.E. Barlow***, U.S. Naval Research Laboratory*, 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. Barnacles adhere to surfaces by a proteinaceous cement, for which most studies to date have been *ex situ* analyses of the protein composition. However, very little is currently known about the chemical structure and composition in the original, undisturbed cement interfaces of barnacles (primary cement interfaces) that provide the strong adhesion to substrates in marine environments. We will present a method that has been implemented for characterizing primary cement interfaces of barnacles using *in situ* attenuated total reflection - Fourier transform infrared spectroscopy (ATR-FTIR). Primary cement of the barnacle *Balanus amphitrite* (= *Amphibalanus amphitrite*) was characterized without any disruption to the original cement interface, after settling and growing barnacles directly on double side polished germanium wafers. High quality IR spectra were acquired of live barnacle cement interfaces, providing a spectroscopic fingerprint of cured primary cement *in vivo* with the barnacle adhered to the substrate. Additional spectra were also acquired of intact cement interfaces for which the upper portion of the barnacle had been removed leaving only the base plate and cement layer attached to the substrate. This allowed further characterization of primary cement interfaces that were dried or placed in D 2 O. The resulting spectra were consistent with a proteinaceous cement, and allowed analysis of the protein secondary structure and water content in the cement layer. The estimated secondary structure composition was primarily b-sheet, with additional a-helix, turn, and unordered components. The cement of live barnacles, freshly removed from seawater, was estimated to have a water content of 20% - 50% by weight. These results provide new insights into the chemical properties of the undisturbed barnacle adhesive interface. The ATR-FTIR method presented is also expected to be useful for *in situ* and *in vivo* studies of bioadhesives from other organisms.

Electronic Materials and Processing Room: B1 - Session EM-TuA

High-K Dielectrics on High Mobility Substrates

Moderator: R.M. Wallace, University of Texas at Dallas

2:00pm **EM-TuA1 Process Evaluation for InGaAs n-Channel MOS Device**, *N. Goel,* Intel Assignee at SEMATECH, ***J. Huang***, SEMATECH, *H. Zhao,* University of Texas-Austin*, I. Ok,* SEMATECH*, J. Lee,* University of Texas-Austin*, P. Majhi,* Intel Assignee at SEMATECH*, P.D. Kirsch*, SEMATECH **INVITED**

With the fundamental limits to the aggressive device scaling in Si CMOS technology, there is significant ongoing research exploring alternate channel materials such as III-V and Ge. These materials hold promise to produce more power efficient transistors compared to current silicon technology. Due to their high carrier mobility, compound III-V semiconductors such as InGaAs and InSb, are being investigated in surface as well as buried channel devices where the inversion or majority carriers determine the device characteristics, respectively. The success of III-V in potential CMOS technology depend on heterogeneous integration on silicon with thinner buffer layers; compatible, low leakage and thermally stable gate dielectric with low interface state density; as well as defect free junctions with low external or access resistance. In addition it is key to develop, standardize and orient various physical and electrical characterization techniques to probe and evaluate the interface and bulk characteristics effectively and correctly at the atomic level. Significant amount of promising research is being done in these modules and there still remain several opportunities to reduce parasitic contributions.

2:40pm **EM-TuA3 Band Alignment at High-κ/III-V Interfaces Grown by Atomic Layer Deposition**, ***A. Wan***, *D. Mastrogiovanni, L. Yu, H.D. Lee, T. Feng, E. Garfunkel, T. Gustafsson,* Rutgers University*, M. Xu, P. Ye*, Purdue University

Band offsets and Fermi level pinning are extremely important issues for metal-oxide-semiconductor (MOS) device structures. In particular, there is increased interest in III-V semiconductor/ high-κ dielectric materials as a future replacement to conventional Si-based complementary MOS technology. In this work, we present band alignment measurements of Al2O3 grown by atomic layer deposition (ALD) on n-GaAs and p-GaAs by combined x-ray (XPS) and ultraviolet (UPS) photoemission spectroscopy. Influence of processing conditions (pre-growth, during growth, and post-growth) and substrate orientation on the Fermi level pinning is discussed. Pinning effects are more problematic on n-GaAs than p-GaAs, due in part to the fact that n-GaAs more readily forms As oxides that have been attributed to high interface gap state densities that cause pinning. Interestingly, at the first few layers of ALD grown at "self cleaning" conditions,[1, 2] native oxides on the GaAs for both n-type and p-type are significantly reduced, but the interfaces on n-GaAs are still strongly pinned. Best results for un-pinning of the Fermi levels between n-GaAs and p-GaAs is observed for Al2O3 / GaAs(111) samples having clean interfaces, grown at condition, and post-deposition annealing at 600° C in forming gas.

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

2. H.D. Lee, T.F., L. Yu, D. Mastrogiovanni, A. Wan, T. Gustafsson, and E. Garfunkel, Appl. Phys. Letters (submitted), 2009.

3:00pm **EM-TuA4 Reduction of Native Oxides on GaAs during Atomic Layer Deposition of Al_2O_3**, ***H.D. Lee***, *T. Feng, L. Yu, D. Mastrogiovanni, A. Wan, T. Gustafsson, E. Garfunkel*, Rutgers University

The integration of high-*k* dielectrics with high mobility III-V semiconductors is important due to the need for higher speed and lower power electronic devices than are offered by Si-based technologies. While high-*k* dielectric deposition on GaAs and InGaAs semiconductors appears particularly promising, the removal of native oxides and the growth an ideal dielectric layer remains a serious challenge. This obstacle arises in part from the high density of defects present at most GaAs-dielectric interfaces, and is related to Fermi-level pinning at the interface. Several groups have shown that chemical cleaning and subsequent passivation of the interface prior to dielectric deposition can greatly reduce the interface state density (D_{it}). However, few passivation solutions are practical for future large scale CMOS device manufacturing.

Although several studies (including our own) have shown the reduction of native oxides on GaAs and InGaAs during atomic layer deposition (ALD) of dielectrics, detailed structural and chemical information about the interface and reduction process have not been reported. We have examined depth profiles of the elements in native oxides and ALD-deposited Al_2O_3 layers on GaAs substrates with an integrated tool that enables ALD growth with *in situ* characterization by medium energy ion scattering spectroscopy (MEIS). Films were also analyzed by x-ray photoelectron spectroscopy (XPS).

We will present data on the reduction of surface "native" oxides from GaAs substrates following reactions with trimethylaluminum (TMA) precursor. MEIS and XPS measurements after one single TMA pulse without oxygen exposure show that ~65% of the native oxide including ~75% of the As oxides are reduced, and a 5Å oxygen rich aluminum oxide layer is formed. XPS also shows that 3 additional TMA pulses reduce all As oxides to a level below our detection limit, and the Ga oxides were also reduced substantially. Further MEIS study of Al_2O_3 grown with the normal atomic layer deposition cycles of TMA and water shows that the growth rate of Al oxide during the reduction of native oxides is faster than the rate after the reduction. The preferential interface reduction of native oxides (especially AsO) helps create a higher capacitance, lower interface defect density CMOS gate stack.

4:00pm **EM-TuA7 Arsenic-dominated Chemistry in the Acid Cleaning of InGaAs and InAlAs Surfaces**, ***Y. Sun***, Stanford Synchrotron Radiation Lightsource*, P. Chen, M. Kobayashi, Y. Nishi,* Stanford University*, N. Goel, M. Garner, W. Tsai,* Intel Corp.*, P. Pianetta*, Stanford Synchrotron Radiation Lightsource

The surface cleaning of InGaAs and InAlAs is studied using Synchrotron Radiation Photoelectron Spectroscopy. Thermal annealing at $400^{o}C$ can not completely remove the native oxides from those surfaces. Elemental arsenic build-up is observed on both surfaces after acid treatment using HCl, HF or H_2SO_4 solutions, which is similar to acid-cleaned GaAs surface. Cleaned InGaAs surface is oxide free but small amount of aluminum oxide remains on cleaned InAlAs surface. The common chemical reactions between III-As semiconductors and acid solutions are identified and are found to be dominated by arsenic chemistry.

4:20pm **EM-TuA8 Wet Treatment for Se Surface Passivation of GaAs and Ge for Advanced CMOS Applications***,* ***F.S. Aguirre-Tostado***, CIMAV-Monterrey, México*, A. Herrera-Gómez,* CINVESTAV-Qro, México*, R.M. Wallace*, University of Texas at Dallas

Surface passivation of III-V and Ge semiconductors is a remaining problem to realize CMOS scaling beyond the 22 nm technology node. Zinc-blende and diamond structure (100) surfaces could be passivated with a single monolayer of divalent atoms like S or Se. In this presentation we show a wet chemical treatment method for the passivation of III-V and Ge (100) substrates with Se and S. The treatment consisted of the dipping of the substrates on a dilution of metallic Se into a 22% ammonium sulfide solution. The treated surface showed 3D structures that are attributed to either clustering during the treatment or during the N2 drying step. AFM, SEM and XPS were used to analyze the surface morphology of the passivation layer and chemical bonding with the substrate atoms. C-V and J-V characteristics of MOS capacitors with and without Se passivation are discussed.

4:40pm **EM-TuA9 The Effect of "Self-Cleaning" ALD Growth on the Electrical Properties of Metal/ High- κ /GaAs and Metal/high-κ/Ge Metal/ MOS Capacitors**, ***L. Yu***, *H.D. Lee, T. Feng, D. Mastrogiovanni, A. Wan, T. Gustafsson, E. Garfunkel*, Rutgers University

The ideas of using high-κ dielectrics as gate oxide and high mobility semiconductor as channel material are promising means of prolonging the scaling of CMOS technology to post Silicon era. However, it has been extremely challenging to produce a high quality oxide/channel interface that yields sufficient device performance for future CMOS. The unwanted chemical species such as residue native oxide, surface carbon, and hydro-carbon can result in defect states at the interface or inside dielectrics. These states can enhance carrier scattering and degrade device threshold voltage. Several recent studies, including ours, showed that, above certain temperature, volatile metal-organic precursors such as TMA can chemically react with the native oxides on the GaAs or InGaAs surface, result in effective removal of native oxide species, and chemically clean interface. This effective is known as the "self-cleaning" ALD growth. Previous studies are largely based on *in situ* XPS and MEIS measurements on ALD grown samples at various stages during the first few cycles. In this work, we will report on the effect of "self-cleaning" ALD growth and post ALD forming gas annealing on the electrical properties of metal/Al_2O_3/GaAs MOS capacitors. We found the combination of the two treatments can significantly enhance the device C-V characteristics. Our preliminary results showed that frequency dispersion of ~2% per decade in the accumulation capacitance and interface state density (D_{it}) of ~5x10^{12} eV^{-1} can be achieved. We also correlated the electrical result with XPS and MEIS studies of the ALD grown Al_2O_3 films and as well as electronic structure at Al_2O_3/GaAs interface. We will also report on the "self-cleaning" growth study of high-κ (Al_2O_3 and HfO_2) on Ge substrate and corresponding electrical result on MOS-CAPs.

5:00pm **EM-TuA10 Characterization of the "Clean-Up" of the Germanium Surface by ALD using Trimethyl Aluminum and Water**, ***M. Milojevic***, University of Texas at Dallas, *R. Contreras-Guerrero, M. Lopez-Lopez*, CINVESTAV-IPN, Mexico, *J. Kim, R.M. Wallace*, University of Texas at Dallas

The "clean-up" effect on III-V substrates has recently been well documented.[1] For the purpose of this study the "clean-up" of Ge oxides by ALD is explored using XPS. By interrupting the ALD process following individual precursor pulses for in-situ monochromatic XPS analysis the reaction mechanisms can be studied in unprecedented detail. As in the case of III-V substrates native germanium oxides are found to be reduced strongly by TMA. Interestingly if the sample is treated with a plasma nitridation technique a GeON layer is grown that appears impervious to this reaction. This is not unexpected given the reports of the stability of GeON formed by ion rather than radical based plasma processes.[2] Oxide free germanium surfaces behave analogously to a surface with initial native oxides since they are oxidized measurably prior to the first TMA pulse due to residual oxidants in a commercial ALD chamber. The unique aspect of the TMA driven "clean-up" is exposed when comparing it to the reduction of interfacial oxides by a thin metallic aluminum layer.[3,4,5,6] In this case in addition to the reduction of germanium oxides the aluminum layer also results in Ge-Al bond formation. In contrast "clean-up" of the oxide by TMA is characterized by a preferential reduction of higher oxidation states of germanium and the absence of any detectable reduction products on the surface.

This work was supported by the FCRP Focus Center on Materials, Structures and Devices and the Texas Enterprise Fund.

REFERENCES

[1] Milojevic, et al., APL 93 (2008) 202902.

[2] Sugawara et al., J. Vac. Sci. Technol. B 2(5), Sep/Oct 2006.

[3] Larsson et al., J. Vac. Sci. Technol. A 7(3), May/June 1989.

[4] Waite et al., J. Vac. Sci. Technol. A 11(4), July/Aug 1993.

[5] Oshima et al., Vac. Sci. Technol. A 12(2), Mar/Apr 1994.

[6] Margaritondo et al., J. Vac. Sci. Technol. A 1(2), Apr/Jun 1983

5:20pm **EM-TuA11 Processing Controlled Substrate Reactions for Deposition of Monoclinic Textured HfO_2 Thin Films on Pre-Oxidized and Nitrided Ge (001) Substrates**, *K.B. Chung, L. Miotti,* ***K.P. Bastos***, North Carolina State University, *D. Nordlund*, Stanford Synchrotron Research Lightsource (SSRL), *G. Lucovsky*, North Carolina State University

2 nm thick films of HfO_2 have been deposited on Ge(001) substrates by remote plasma chemical vapor deposition for (i) multiple etching cycles in dilute HF followed by distilled water rinsing, and (ii) an in situ remote plasma-assisted nitridation (RPAN) process. In a second set of studies, the step(i) pre-clean was replaced by a basic re-clean using methanol and NH_4OH. Studies by X-ray absorption spectroscopy (XAS) in O and N K edge regimes, were used to monitor HfO_2 nano-grains morphologies. Previous studies indicated epitaxial textured HfO_2 and TiO_2 films were obtained on Ge(001) surfaces. However, these studies were based on a recipe that worked, and did provide insights to significant connections between pre-cleaning and post deposition annealing. We have found two aspects of processing are crucial, and these were evaluated spectroscopically. Electrically active defects in metal-oxide-semiconductor test devices indicated high-defect densities correlated directly with Ge and O reacting with HfO_2 in the interfacial transition region, resulting in mixed-morphology grains.

Interfacial and bulk film degradation are also detected in XAS O K edge measurements. The occurrence of a monoclinic (m-)HfO_2 E_g edge structure is associated with Ge-O free interfacial transition regions. Ge-O interfaces results in tetragonal (t-)HfO_2, or mixtures of t-HfO_2 and m-HfO_2 grains. Acidic and basic pre-cleans each followed by an RPAN process prevented reactions between Ge-O surface bonding and plasma-excited HfO_2 precursors, consistent with textured m-HfO_2 films. Spectroscopic ellipsometry indicated that Ge-O bonding was significantly higher for acidic pre-cleans compared with basic pre-cleans. Post deposition annealing cycles with textured m-HfO_2 films were consistent with this difference. Two step annealing after the acidic clean, the first at 550°C in Ar, and the second at 800°C in Ar, resulted in textured m-HfO_2 directly in contact with a reconstructed Ge(001) surface. N K edge XAS, had previously indicated complete release of N after annealing to 700°C in Ar. In contrast, with less Ge-O interfacial bonding in the basic pre-clean, Ge-O and Ge-N interfacial bonds were eliminated sequentially during an 800°C anneal in Ar. O K edge XAS for HfO_2 with the X-ray polarization in the direction of the dimer rows of Ge(001) wafers, or perpendicular to that direction indicated similar textured growth. This is consistent with the textured m-HfO_2 films having nano-grains aligned at ±45^{o} relative the dimer row direction.

Exhibitor Workshops
Room: Exhibit Hall 1 - Session EW-TuA

Exhibitor Workshop
Moderator: B.R. Rogers, Vanderbilt University

3:20pm **EW-TuA5 Ztherm™ Modulated Thermal Analysis with Sub-Zeptoliter Resolution Using the Asylum Research Cypher and MFP-3D AFMs**, ***J. Li***, *R. Proksch*, Asylum Research

Asylum Research, the technology leader in Scanning Probe and Atomic Force Microscopy (SPM/AFM) will present the new *Z*therm Modulated Local Thermal Analysis Option for its MFP-3D™ and Cypher™ AFMs. *Z*therm provides highly localized heating with sensitivity to $\leq 10^{-22}$ liter (sub-zeptoliter) materials property changes, more than an order of magnitude improvement in volume over that previously available with commercial systems. A standing problem with existing AFM-based thermal analysis systems is thermally induced bending of the cantilever that results in spurious deflection signals and variable loads being applied during heating. Asylum has developed a patent-pending cantilever compensation and control solution that corrects this problem, providing constant-load detection of thermally induced melting (Tm), phase transitions (Tg) and other morphological and compliance effects for materials studies and material identification – for areas less than 20nm x 20nm. In addition to standard thermal analysis capabilities, the *Z*therm package can also be used to evaluate contact stiffness and dissipation as a function of temperature with advanced techniques such Dual AC Resonance Tracking (DART™). The contact stiffness and dissipation – measured at the cantilever resonance – are much more sensitive to temperature dependent properties, including surface melting and transition temperatures, than conventional deflection-based measurements. In addition, integrated piezo actuation allows high resolution AC imaging of samples for surface topographical mapping before and after thermal measurements.

3:40pm **EW-TuA6 Difference Raman for Enhancing Image Resolution by Accurate Tip Positioning of an Atomic Force Probe that Enhances or Shadows the Raman Signal**, *J. Ernstoff,* ***R. Dekhter***, *H. Taha, A. Israel, D. Lewis,* Nanonics Imaging Ltd., Israel, *A. Lewis*, Hebrew University of Jerusalem, Israel

Tip enhanced Raman scattering (TERS) has been shown as a potential technique for overcoming limitations of conventional micro Raman spatial resolution and for other apertureless near-field optical measurements based on plasmonic interactions. In this talk we will compare the resolutions obtainable by such plasmonic enhancement techniques as compared to a method we have developed based on the ultra-sensitive nature of difference Raman. In this latter technique an AFM probe with an exposed tip geometry that is optimized to block a nanometric region of a sample will be used in conjunction with difference Raman to obtain significant improvements in Raman image resolution over conventional far-field scattering. For this new imaging protocol one has to have not only exposed tip geometries but also an AFM system that can modulate and scan the probe independently of the sample scanning required for Raman imaging systems. The tip scanning is required for optimizing the position of the probe tip for maximizing the shadow effect on the sample in the near-field. The independent tip movement is required for bringing the probe in and out of the near-field of the sample so that a difference Raman can be recorded at each pixel and an image formed as the sample is scanned point by point. All of the above in terms of the Shadow protocol are predicated by having an AFM system that has a completely free optical axis from above and is completely independent from the lens of the micro-Raman. Results will be shown on structured thin films of strained silicon on silicon to show the relative fidelity of these imaging modalities. The results indicate that Shadow Near Field Scanning Optical Microscopy (sNSOM) is a powerful technique that can be applied for significant improvements in Raman imaging spatial resolution.

Graphene Topical Conference
Room: C3 - Session GR+TF-TuA

Graphene: Characterization, Properties, and Applications
Moderator: M. Fuhrer, University of Maryland, College Park

2:00pm **GR+TF-TuA1 Graphene Atomic Membranes**, ***P.L. McEuen***, Cornell University **INVITED**

Atomically thin graphene membranes have exceptional electronic, optical, thermal and mechanical properties. Here we discuss our group's measurements on graphene membranes made by either exfoliation, epitaxial growth on SiC, or chemical vapor deposition growth on Ni or Cu. For example, we demonstrate that a monolayer graphene barrier is impermeable to standard gases, including helium. By applying a pressure difference across the membrane, we measure both the elastic constants and the mass. We also discuss mechanical resonators made from graphene, as well as the photocurrent response of graphene optoelectronic devices. We find the photoresponse at a graphene interface junction is photo-thermoelectic, i.e. the laser locally heats the graphene, giving rise to a thermoelectric response. This is in contrast to previous interpretations based on photovoltaic charge carrier separation at local potential variations in the sample. The photo-thermoelectric model accurately describes the temperature and laser power dependence, and also provides a simple way to probe the thermal conductivity of graphene membranes. Work done in collaboration with Scott Bunch, Arend van der Zande, Scott Verbridge, Xiaodong Xu, Nathaniel Gabor, Shriram Shivaraman, Xun Yu, Robert Barton, Jonathan Alden, Lihong Herman, MVS Chandrashekhar, Jiwoong Park, Jeevak Parpia, Harold G. Craighead, and Michael G. Spencer

2:40pm **GR+TF-TuA3 Impact of Argon on the Growth of Epitaxial Graphene**, ***J.L. Tedesco***, *R.L. Myers-Ward, G.G. Jernigan,* U.S. Naval Research Laboratory, *J.A. Robinson,* The Pennsylvania State University, *J.C. Culbertson, P.M. Campbell, J.K. Hite, C.R. Eddy, Jr., D.K. Gaskill*, U.S. Naval Research Laboratory

Epitaxial graphene (EG) grown *in vacuo* on semi-insulating, on-axis 4H- and 6H-SiC substrates has demonstrated morphological problems [1], such as pitting in C-face substrates during *in vacuo* growth. In order to reduce the nonuniformities present in the EG, films were grown in an Ar ambient and compared to *in vacuo* films using substrates sourced from the same wafers. The growths took place in a commercial Aixtron VP508 hot-wall epitaxial SiC growth reactor. The Ar growths were performed using temperatures ranging from 1,500°C to 1,600°C and pressures ranging from 50 to 200 mbar. The *in vacuo* growths took place for temperatures ranging from 1,225°C to 1,700°C and pressures ranging from 10^{-3} to 10^{-6} mbar. The resulting films were characterized with Nomarski and atomic force microscopies, Raman and x-ray spectroscopies, and Hall effect measurements.

Si-face EG films did not form under Ar at temperatures $\leq$ 1,500°C, yet *in vacuo* films formed for temperatures above ~1,400°C. At temperatures > 1,500°C under Ar, graphene was successfully grown and, while the morphology was not significantly different from *in vacuo* films, Raman spectroscopy measurements indicated that EG films with improved thickness and strain uniformity were realized. At an Ar growth pressure of 50 mbar, resulting Si-face EG was mostly bilayer graphene, while at 200 mbar, the resulting EG films were predominantly monolayer graphene. X-ray photoelectron spectroscopy measurements indicated that argon-grown EG was thinner than *in vacuo* EG grown at the same temperature.

The morphology of argon-grown C-face films was markedly different from *in vacuo* films. Under Ar, graphene did not grow below 1,500°C, while *in vacuo* films began to grow at 1,225°C. For growths at temperatures > 1,500°C, the density of substrate pits was reduced significantly and was eliminated in half of the argon-grown films. Furthermore, at temperatures between 1,500°C and 1,600°C, ambient-controlled films were incomplete, and the percentage of the substrate covered by graphene increased with growth temperature.

Growth under Ar improved the electrical properties for films on both faces. Mobilities increased by up to 4 times relative to *in vacuo* films, while carrier densities decreased by ~10 times. For both *in vacuo* and argon-grown EG, the carrier densities of Si-face EG were at least an order of magnitude less than those of C-face EG films. Furthermore, Hall effect measurements showed that, while *in vacuo* EG films on both faces were divided between n-type and p-type, argon-grown Si-face EG was generally n-type while argon-grown C-face EG was generally p-type.

[1] B.L. VanMil, *et al*., Mater. Sci. Forum **615-617**, 211 (2009).

3:00pm **GR+TF-TuA4 Mapping the Electronic Surface Potential of Graphene Grown on Ir(111) and Ru(0001)**, *S. Barja,* ***B. Borca***, Universidad Autónoma de Madrid, Spain, *M. Garnica,* IMDEA Nanociencia, Spain, *F. Hermanns, J.J. Hinarejos,* Universidad Autónoma de Madrid, Spain, *A.L. Vazquez de Parga, R. Miranda*, UAM & IMDEA Nanociencia, Spain

Moiré patterns are generated by the superposition of two periodic structures with a lattice mismatch. They have been observed by means of Scanning Tunneling Microscopy (STM) on different systems and their interpretation, in some cases, is not straightforward. The influence, at the atomic scale, of these patterns in the local density of states of the overlayer is not clear and can be studied by STM.

The growth of graphene on metallic substrates allow us not only control the periodicity of the Moiré pattern but also tailor the interaction strength between the carbon atoms and the metallic substrate [1]. In this work we compare the results obtained on graphene overlayers grown on two different metallic substrates. We studied graphene/Ir(111) and graphene/Ru(0001) in the former there is a weak interaction between the graphene overlayer and the substrate and in the later the strength of the chemical interaction is modulated by the Moiré pattern.

Field Emission Resonances (FERs), which are detected by STM when applying voltages larger than the work function, can be used to explore with nanometer resolution, the inhomogeneities in the local surface potential landscape. Operating the STM in constant current mode implies a constant electric field between tip and sample and the expected energy position for the FERs is given by the expression founded by Gundlach some time ago [2]. From that expression it is possible to determine experimentally the local work function of the surface. We applied this method to the Moiré pattern formed by graphene grown on Ir(111) and Ru(0001). For graphene on Ir(111) we did not find any modulation in the work function due to the Moiré pattern. On the contrary for graphene on Ru(0001) we have found a difference of 0.25 eV in the work function values depending on the position on the Moiré pattern. For graphene on Ru(0001) we also found that the energy position of the first FER presents strong spatial variations that can be measured by scanning tunneling spectroscopy. In fact, for the grahene/Ru(0001) system, the energy position of the first FER is not easily related with the local work function and is modified by the interaction between graphene and the Ruthenium underneath. The energy position of the higher FERs is only influenced by the variations in the local work function.

[1] A.B. Preobrajenski *et al*., Phys. Rev. B **78,** 073401 (2008)

[2] K.H. Gundlach, Solid State Electron. **9**, 949 (1966)

4:00pm **GR+TF-TuA7 Graphene Electronics and Optoelectronics**, ***P. Avouris***, IBM T.J. Watson Research Center **INVITED**

Graphene is a single atomic layer, 2-dimensional zero band-gap semiconductor with a high Fermi velocity and a huge electrical mobility approaching 200,000 $cm^2/V\cdot s$ for a free sheet. The photonic properties of graphene are equally remarkable: the strength of light-graphene interaction over a very wide range of photon energies is 10 to 100 times stronger than that in conventional semiconductors. These unique properties can be employed in both electronic and photonic applications. In my talk I will discuss the basic device physics, fabrication and operating characteristics of high frequency, single layer graphene transistors. Devices with gain up to 50GHz will be demonstrated. I will also present the physics and device results on single and few layer graphene ultra-high bandwidth photodetectors appropriate for optical communications, imaging and other applications.

4:40pm **GR+TF-TuA9 Graphene Growth on Metal Surfaces**, *E. Loginova, N.C. Bartelt, P.J. Feibelman,* ***K.F. McCarty***, Sandia National Laboratories

Previous work has shown that when elemental carbon is deposited on the Ru(0001) surface, graphene forms from a dense, tightly-bound carbon-adatom gas. Nonlinearity of the graphene growth rate with carbon adatom density suggests that growth proceeds by addition of carbon atom clusters to the graphene edge [1,2]. In this talk, we present the results of low-energy electron microscopy (LEEM) observations of graphene formation when Ru(0001) and Ir(111) surfaces are exposed to ethylene. We find that graphene growth velocities and nucleation rates on Ru have precisely the same dependence on adatom concentration as in elemental carbon deposition [3]. Thus, hydrocarbon decomposition only affects graphene growth through the rate of adatom formation; for ethylene, that rate decreases with increasing adatom concentration and graphene coverage. Graphene growth on Ir(111) is similar to that on Ru: the growth velocity is the same nonlinear function of adatom concentration (albeit with much smaller equilibrium adatom concentrations, as we explain with DFT calculations of adatom formation energies). When graphene is exposed to oxygen at high temperatures, it is etched. We observe the etching to proceed by the inverse of the graphene growth mechanism, i.e., by cluster detachment.

[1] E. Loginova, N. C. Bartelt, P. J. Feibelman, and K. F. McCarty, *Evidence for graphene growth by C cluster attachment*, New Journal of Physics 10 (2008) 093026

[2] K. F. McCarty, P. J. Feibelman, E. Loginova, and N. C. Bartelt, *Kinetics and thermodynamics of carbon segregation and graphene growth on Ru(0001)*, Carbon doi:10.1016/j.carbon.2009.03.004

[3] E. Loginova, N. C. Bartelt, P. J. Feibelman, and K. F. McCarty, *Factors influencing graphene growth on metal surfaces*, submitted to New Journal of Physics (2009).

5:00pm **GR+TF-TuA10 The Reduction Kinetics of Graphene Oxide Determined by Temperature Programmed Desorption**, ***C.A. Ventrice***, *N.J. Clark, D.A. Field,* Texas State University, *I. Jung, D. Yang,* University of Texas, *H. Geisler,* Texas State University, *R.D. Piner, R.S. Ruoff,* University of Texas

Graphene oxide, which is an electrical insulator, shows promise for use in several technological applications. For instance, individual, monolayer, graphene oxide platelets could be used as dielectric layers in nanoscale electronic devices. Since the electrical, optical, and mechanical properties of graphene oxide can be controlled by chemical modification, films composed of layers of graphene oxide platelets may be used as the active region of chemical sensors. In principle, graphene oxide films could also be used as a precursor for the formation of large-scale graphene films by either thermal or chemical reduction of the graphene oxide. In order to determine the thermal stability and reduction kinetics of graphene oxide, temperature program desorption measurements have been performed on multilayer films of graphene oxide deposited on SiO2/Si(100) substrates. The graphene oxide was exfoliated from the graphite oxide source material by slow-stirring in aqueous solution, which produces single-layer platelets with an average lateral size of ~10 μ m. From the temperature programmed desorption measurements, it was determined that the primary desorption products of the graphene oxide films for temperatures up to 300 ° C are H_2O, CO_2, and CO, with only trace amounts of O_2 being detected. Since carbon is lost during the reduction process in UHV, the addition of other carbon containing reactants during the thermal reduction will be needed to regain the electrical and mechanical properties of pristine graphene. An activation energy of 32 ±4 kcal/mol (1.4 eV/molecule) was determined by assuming an Arrhenius dependence for the decomposition process.

5:20pm **GR+TF-TuA11 Covalently Immobilized Graphene: Fabrication, Characterization, and Applications**, ***M. Yan***, *L.-H. Liu, G. Nandamuri, R. Solanki*, Portland State University

We developed a simple method for the covalent immobilization of graphene films on solid substrates using a heterobifunctional coupling agent. The films were robustly attached to the substrate, withstanding extensive solvent extraction and sonication. Large sheets of single and few-layer graphene films were fabricated and characterized with Raman, AFM, and XPS. The method is readily applicable for the fabrication of graphene microarrays. Transistors were also constructed with these materials. The device performance with regard to surface and interface properties will be discussed in this presentation.

Nanometer-scale Science and Technology
Room: A8 - Session NS1+PV-TuA

Organic Photovoltaics I
Moderator: P. Sharps, Emcore Corporation

2:00pm **NS1+PV-TuA1 Probing Polymer Photovoltaics: Imaging Photocurrents and Controlling Morphology in Organic Solar Cells**, ***D.S. Ginger***, University of Washington **INVITED**

Organic solar cells are a potential low-cost alternative to conventional inorganic photovoltaics. The most successful organic solar cells rely on nanoscale phase separation between different components to achieve high efficiencies. Understanding and controlling nanoscale film structure has thus become the central challenge that affects every aspect of the field, from the optimization of new low-bandgap polymers to early efforts to scale up manufacturing of polymer solar cells. Our group has pioneered several scanning-probe methods, including time-resolved electrostatic force microscopy (trEFM) and photoconductive atomic force microscopy (pcAFM), as tools to characterize active organic solar cells. We discuss applications of these tools to study several model polymer systems, including the local origin of the photocurrent in polyfluorene blends, the effect of annealing on the formation of hole transport, electron transport and photocurrent collection networks in the archetypal polythiophene (P3HT) fullerene (PCBM) system, and the role that mesoscopic PCBM crystallites play in polyfluorene-copolymer/PCBM cells during solvent-vapor annealing. These data show the power of scanning-probe methods in correlating morphology with performance, and underscore the need to model these devices as fully 3D networks, rather than as uniform 2D semiconductor slabs.

2:40pm **NS1+PV-TuA3 Nanoscale Confinement Induced 3-D Chain Alignment of Poly (3-hexylthiophene) for Organic Solar Cells**, ***M. Aryal***, *K. Trivedi, W. Hu*, University of Texas at Dallas

Organic semiconducting polymers are of wide interests for many applications in organic solar cells, field effect transistors, light emitting diodes, and biosensors. The optical and electrical properties of these polymers are anisotropic which largely depends on their nanoscale morphology, crystallinity and the direction of chain configuration. Furthermore, control over direction of chain orientation is essential as certain devices prefer chain alignment in certain directions as determined by device structures, e.g. vertical alignment for solar cells where vertical charge transport occurs, while for FETs, lateral orientation along the channel is preferred instead. Though the significant progress has been made by the development of varieties of techniques for control of nanoscale morphology, crystallinity and orientation of polymer chains for years, the perfect crystallization and preferred chain ordering in nanoscale regime still remains challenging. We report the fabrication of highly-ordered nanostructure arrays of nanopillars and nanogratings in poly (3-hexylthiophene) (P3HT) using nanoimprint lithography and show 3-D chain ordering by x-ray diffraction (XRD) analysis. We have proved for the first time that nanoscale confinement exerted by the mold can induce only one possible configuration of the chain network in the three dimensional P3HT nanostructures during thermal nanoimprint process. Such monodical 3-D chain configuration strongly depends on the geometry of the nanoconfinement. Interestingly the configuration is arranged in a favorable way for solar cell and FET applications, e.g. vertical chain alignment, and π-stacking along gratings.

In this report, uniform 80 nm thin films of rerioregular P3HT were prepared on a Si substrate. The nanograting of 200 nm height, 65 nm wide gratings at a period of 200 nm while hexagonal array of nanopillars of 150 nm high nanopillars with 80 nm diameter were fabricated using nanoimprint lithography. The P3HT nanostructures were characterized by SEM and crystallization and chain orientation were studied by both in-plane, out-of-plane and in-plane grazing incident XRD. The chain ordering of thin film, nanopillar and nanograting structures are proved to be entirely different. The conjugated polythiophene backbones which are horizontal to the substrate in the thin film are reordered into vertical direction in the imprinted structures of P3HT. The interaction of hexyl side chains with hydrophobic mold surface in turn results π-stacking along nanogratings. We will present XRD results analysis and expect to present solar cell device results using these imprinted P3HT nanostructures.

3:00pm **NS1+PV-TuA4 Porphyhrin-Gold Junctions in Molecular Optoelectronics**, ***S.U. Nanayakkara***, University of Pennsylvania, *P. Banerjee,* University of Maryland, *D. Conklin,* University of Pennsylvania, *T.-H. Park,* University of Michigan, *M.J. Therien,* Duke University, *D.A. Bonnell*, University of Pennsylvania

Photo-conductance in novel multi-chromophoric molecules with porphyrin centers has been measured. This class of molecules is fully conjugated optical absorption properties that induce hole mediated conductivity with delocalization lengths on the order of 8 nm. Conjugated linker groups that terminate with a thiolate functionality (on one or both sides of the molecule) enable facile, co-valent attachment to a gold surface. We have attached these multi-chromophoric molecules between surface-bound Au nanoparticles and have measured transport as a function of varying laser excitation wavelengths. Additionally, we have measured spatially varying, charge transport in individual molecules within a tunneling junction utilizing a laser-coupled ultra-high vacuum scanning tunneling microscope. The wavelength dependent conductance will be discussed within the context of the molecule-Au junction.

4:00pm **NS1+PV-TuA7 Torsional Defects in Conjugated Polymers: Modeling and Nanostructured Photovoltaic Materials**, ***S.B. Darling***, *M. Sternberg*, Argonne National Laboratory **INVITED**

Conjugated polymers represent a promising class of organic semiconductors with potential applications in a variety of molecular devices. Poly(3-alkylthiophene)s, in particular, are garnering interest due to their large charge carrier mobility and band gap in the visible region of the spectrum. Defects play a pivotal role in determining the performance of polymer electronics, and yet the function of specific types of defects is still largely unknown. Density functional theory calculations of alkyl-substituted oligothiophenes are used to isolate the effect of static inter-ring torsion defects on key parameters such as electronic coupling between rings and band gap. These polymers are often modeled with very short backbones and without their side chains. These results demonstrate the shortcomings of this approach for modeling torsional disorder and identify a minimal acceptable model.[1] Two experimental systems, one based on block copolymers and the other on a hybrid oxide nanotube-polymer system, with nanoscale morphology rationally designed to minimize torsional disorder will also be discussed. Results have potential implications both for the fundamental understanding of intramolecular charge transport and for improving processing in organic optoelectronic devices.

[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.

5:00pm **NS1+PV-TuA10 Locally Probing the Efficacy of Photoinduced Charge-Generation and Trap Clearing in Pentacene-Based Thin-Film Heterojunctions and Transistors using Electric Force Microscopy**, ***J. Luria***, Cornell University, *A. Gorodetsky, C. Nuckolls,* Columbia University, *J.A. Marohn*, Cornell University

Pentacene and its derivatives are leading candidates for many organic electronics applications including electron donors in organic photovoltaics. Charge trapping, which is associated with device degradation in both photovoltaics and transistors, remains poorly understood even in this comparatively well studied class of materials. Northrup and Chabinyc [1] have carried out ab initio studies showing that reactions of holes with hydrogenated and oxygenated pentacene is a plausible charge trapping mechanism. Jaquith et al. [2] demonstrated a dependence of trap formation rate on hole concentration in pentacene, which is consistent with traps forming by a defect-mediated chemical reaction, and showed that traps could be cleared by the application of light. Coffey and Ginger [3] have shown that the fastest charging rates under illumination in polymer/fullerene films do not occur at phase interfaces, as widely assumed. Charge generation at the donor-acceptor interface in organic heterojunctions also remains poorly understood.

To resolve such open questions, we have developed a general approach to illuminating samples (from above) in an electric force microscope. We will describe studies where variable-wavelength light is utilized to clear traps in polycrystalline pentacene transistors. We will also discuss investigations into image charge generation in bis(thienyl)-pentacene/PCBM bulk heterojunction thin films.

[1] J.E Northrup and M.L. Chabinyc, *Phys. Rev. B* **68**, 041202 (2003).

[2] M.J. Jaquith, E.M. Muller, and J.A. Marohn, *J. Phys. Chem. B* **111,** 7711 (2007).

[3] D.S. Ginger and D.C. Coffey, *Nat. Mater.* **5**, 735 (2006).

5:20pm **NS1+PV-TuA11 A New Look at Si Inversion-Layer Solar Cells, Meeting Ground for Inorganic, Molecular and Organic Electronics**, ***R. Har-Lavan***, *O. Yaffe, D. Cahen*, Weizmann Institute of Science, Israel

We suggest a near-ambient temperature, simple and potentially low-cost approach to fabricate semiconductor solar cells. To this end we use a monolayer of organic molecules that self-assembles onto n-Si, to passivate and buffer the Si surface. The direct binding of the molecules to the oxide-free Si surface also provides a strong interface dipole and effectively reduces the semiconductor's electron affinity by as much as 0.7 eV. A thin layer of a conducting polymer with a high work function, that is spin-coated on top of the molecular layer plays a threefold role:

the high work function induces inversion in the Si and leads to an n-p^+ homojunction in the Si;

with n~1.5 refractive index the polymer acts as an anti-reflective coating to the Si.

because it protects the molecular monolayer, subsequent metal deposition and encapsulation is now possible.

Good and stable interface passivation along with strong inversion allow minority carriers, generated by absorbed sun light, to move laterally within the inverted Si top layer and to be collected by a minimal area metal grid, deposited on the conducting polymer. For the same reason (lateral conductance) photo-current losses, due to polymer sheet resistance, are minimized. Not only are cells fabricated without high temperature steps, the use of small organic molecules appears to convey here a unique advantage over inorganic passivation or buffer layers. The approach, which includes no or minimal (for metal grid) high vacuum steps, should be applicable to other inorganic absorbers, amorphous materials and thin films to improve photovoltaic solar energy conversion.

5:40pm **NS1+PV-TuA12 Modification and Characterization of Transparent Conducting Oxides for Generation III Nanostructured Photovoltaics**, ***D. Placencia***, *N. Armstrong*, University of Arizona

Indium-Tin oxide (ITO), Indium-Zinc oxide (IZO), and Antimony-doped tin oxide (ATO) substrates were modified with ca. 3-5 nm gold nanoparticles to characterize their effect on the performance of Generation III organic photovoltaics (OPVs). This talk will focus on the presumed mechanism for their deposition, their impact on rates of electron transfer (solution), and OPV device performance parameters. ITO, IZO, and ATO thin films were deposited via magnetron sputtering and modified through a deposition-precipitation protocol. X-ray, UV photoelectron, and polarization modulated infrared reflection absorption spectrocopies were used to characterize the interfacial composition, work function changes, and the molecular nature of Au NP nucleation and growth. Planar heterojunction OPVs were created to evaluate the efficacy of oxide modification with metal nanoparticles, as an intermediate step towards the improvement of charge collection at the organic/oxide interface in organic solar cells.

Nanometer-scale Science and Technology
Room: L - Session NS2-TuA

Templated Self-Assembly
Moderator: N.A. Burnham, Worcester Polytechnic Institute

2:00pm **NS2-TuA1 Size-selective Templated Self-Assembly of Particles**, *C. Kuemin*, ETH Zurich, Switzerland, *E. Loertscher, A. Rey, A. Decker*, IBM Research GmbH, Zurich Research Laboratory, Switzerland, *N.D. Spencer*, ETH Zurich, Switzerland, ***H. Wolf***, IBM Research GmbH, Zurich Research Laboratory, Switzerland

The special properties of nanoscale objects, such as metal and semiconductor nanoparticles, nanowires, or nanotubes, make them promising building blocks of novel optical and electronic devices. The systematic fabrication of devices usually requires the integration of these heterogeneous materials into a larger, ordered structure. More complex device architectures may, in addition, entail the selective assembly of several different types of small objects into pre-defined locations or demand an assembly with the correct orientation when such objects are nonspherical.

Serial pick-and-place techniques are no longer economical at these length scales. Self-assembly mechanisms can arrange a large number of objects in parallel, but will mainly produce homogeneous monolayers limited to the characteristic length-scale of the assembled objects (e.g. the diameter of the particles). Templated assembly on the other hand, provides an adequate strategy for the massively parallel arrangement of particles into designed patterns of arbitrary structure. With selective assembly sites, integration of different components becomes feasible.

Here we show concepts and experimental implementations for the selective templated self-assembly of spherical particles of different size. Particles between 200 and 500 nm in size are assembled selectively into predetermined locations on a template. We use capillary assembly from aqueous suspensions onto templates with topographic features that are selective for a certain particle size. The templates are prepared in poly(dimethylsiloxane) (PDMS) molded from a topographically patterned master. The master is a Si wafer patterned by electron beam lithography.

As a model system for the templated self-assembly of nonspherical objects we use Au nanorods.

2:20pm **NS2-TuA2 Templated Self Assembly of 6 nm Gold Nanoparticles by Means of micro-Trough Technique**, ***L.E. Ocola***, Argonne National Laboratory, *A. Chao*, Illinois Mathematics and Science Academy

This paper demonstrates that combining top-down electron beam lithography and bottom-up colloidal chemical assembly leads to large scale placement of nanoparticles on arbitrary flat substrates. We report on the templated self-assembly of 6 nm gold nanoparticles using template geometries that lend themselves to induce self-assembly at distances significantly larger than typical trench geometry constraints. We can obtain oriented and ordered arrays of 6 nm gold nanoparticles that extend hundreds of nanometers away from any template boundary. The goal is to be able to create oriented arrays of nanoparticles over hundreds of microns. We have developed a micro-Trough technique where we define a specific area on where to create an equivalent of a Langmiur Blodgett trough directly on a sample surface. Using this technique we overcome liquid current effects usually encountered in traditional colloid dispersion deposition techniques. Progress in templated self-assembly will lead to novel nanophotonic and chemical sensing devices, along with the means to extend top-down nanofabrication below the 10 nm barrier.

2:40pm **NS2-TuA3 Focused Ion Beam Templating and Doping of Si(Ge) Nanostructures**, ***J.F. Graham***, *C.D. Kell*, *J.A. Floro,* University of Virginia, *R. Hull*, Rensselaer Polytechnic Institute

An important application of the focused ion beam (FIB) is nanoscale modification of surfaces for directed self-assembly of nanostructures. In previous work, we have demonstrated Ga^+ FIB patterning of Si(100) substrates followed by epitaxial deposition, resulting in templated nucleation of Ge quantum dots (QDs) and SiGe quantum dot molecules (QDMs). Such positional control of QD growth using FIBs should be useful in fabricating potential, QD-based nanoelectronic devices like quantum-dot cellular automata and spin exchange switches. However, since Ga is a *p*-type dopant in Si, patterning with Ga^+ ions from a conventional liquid metal ion source (LMIS) leads to uncontrolled doping of the Si substrate. Moreover, Ga can behave as a surfactant during epitaxial growth of Si and Ge. In this work, we use electrically non-invasive ions for FIB-templated growth in order to avoid Ga doping and as a means to investigate fundamental mechanisms involved in templated nucleation of QDs. We employ a mass-selecting FIB and alloy LMISs to work with ions which are unobtainable from elemental sources. Ions of particular importance for non-invasive patterning include Si (obtained from a AuSi LMIS) and Ge (from a AuGeMn LMIS). In addition, the use of B ions (from an AsPdB LMIS) is explored as a potential method of producing auto-doped, templated QDs. These techniques are establishing a platform for nanoscale control of the formation, position and doping of epitaxial QD arrays of any desired complexity.

4:00pm **NS2-TuA7 Clathrin: A Protein Scaffold for Biotemplating 2-D and 3-D Nanostructures**, ***A.P. Schoen***, *S.C. Heilshorn*, Stanford University

Nature has evolved numerous methods for the self-assembly of nanoscale architectures with high levels of precision. Biomolecules such as DNA, bacterial membranes, viral particles, and proteins all exhibit stunning regularity and reproducibility in the structures they can achieve, making them ideal templates for the patterning of inorganic nanostructures. While some success has been realized in patterning materials from these biological templates, they generally have been limited to simple 0-D or 1-D structures. In contrast, proteins have the ability to form 2-D and 3-D structures, and the immense library of naturally available proteins encourages the development of new techniques to reproducibly template these materials.

Using clathrin as a model protein, we are developing flexible biotemplating protocols to interface protein structures with a variety of inorganic materials. The intracellular transport protein clathrin is composed of three semi-flexible arms that form a pinwheel structure with three-fold symmetry. Clathrin provides a framework that offers access to a variety of architectures, both 2-D and 3-D, such as sheets, tetragons, and geodesic spheres depending on the environmental conditions (pH, concentration, buffer ionic strength) during assembly. The ability of this single protein to assemble into multiple structures makes clathrin an ideal model system for investigating the underlying kinetic and thermodynamic principles of self-assembly. To interface these biological templates with inorganic materials, we design bi-functional peptide linkers that serve as molecular bridges between the clathrin protein and inorganic materials. Rational design of these bi-functional peptide linkers includes a conserved clathrin-binding motif fused to an inorganic-binding peptide sequence. This newly developed strategy enables great flexibility to interface a single protein biotemplate with a variety of different inorganics without requiring any direct modifications to the template. The ability of a single protein biotemplate to assemble into multiple 2-D and 3-D protein nanostructures and to interface with a variety of inorganic materials makes this modular, self- assembling system applicable to a broad range of applications.

4:20pm **NS2-TuA8 Assembly of Block Copolymer Micelles on a Lithographically Modified Surface**, ***A. Pearson***, *R.C. Davis*, Brigham Young University

Block copolymer self-assembly is a promising method of creating ordered arrays with feature sizes smaller than possible by conventional lithography techniques. Block copolymer micelle patterning has proven to be a versatile method of creating hexagonal arrays of metal nanoparticles with sizes less that 10 nm and spacing that can be adjusted by changing the molecular weight of the block copolymer used. In order to use these nanoparticles for many lithographic applications, registration of the nanoparticles with other surface patterns is essential. Here we exploit the self-aligned assembly of PS-P2VP block copolymer micelles with both topographical and chemical surface patterns to achieve micelle registration. Specifically e-beam lithography and plasma etching of SiO_2 surfaces was used to create recessed boxes and ovals where controlled numbers of micelles were deposited by dip coating. Chemical patterning was used to selectively place micelles in the recessed patterns with low micelle adsorption in the non-recessed regions. Gold nanoparticles were formed from the micelles by adding $HAuCl_4$ to the micelles in solution prior to deposition. After dip coating , an oxygen plasma etch removes the polymer, leaving gold nanoparticles. Scanning electron and atomic force microscopy were used to measure nanoparticle alignment.

Plasma Science and Technology
Room: A1 - Session PS-TuA

Fundamentals of Plasma-Surface Interactions I
Moderator: X. Hua, AMAT

2:00pm **PS-TuA1 Correlation between Surface Chemistry and Ion Energy Dependence of the Etch Yield in Multicomponent Oxides Etching**, ***P.-M. Bérubé***, *J.-S. Poirier*, *J. Margot*, *L. Stafford,* Université de Montréal, Canada, *P.F. Ndione*, *M. Chaker*, *R. Morandotti*, INRS-EMT, Canada

Progress in the development of advanced electronic and photonic devices strongly rely on the capability of etching multicomponent oxides such as $Ca_xBa_{(1-x)}Nb_2O_6$ (CBN), (Ba,Sr)TiO_3 (BST), and $SrTiO_3$ (STO) that exhibit ferroelectric and electro-optic properties of interest for these applications. An important issue in the development of plasma etching recipes for multicomponent oxides is that in contrast with simple, binary oxides such as SiO_2, ZrO_2 and HfO_2 the various atoms contained in the films are likely to interact differently with the various reactive species of the plasma. This makes investigations of the underlying physics and chemistry a very difficult task. In the present work, we propose a simple and effective way to examine the influence of surface chemistry on the plasma etching dynamics of multicomponent oxides. This method uses the energy dependence of the etch rate in combination with measurements of the total positive ion flux impinging onto the surface and relative positive ion composition of the plasma. Using pulsed-laser-deposited CBN and STO thin films as examples, it was found that the etching energy threshold, Eth, shifts towards values larger or smaller than the sputtering threshold depending on whether or not ion-assisted chemical etching is the dominant etching pathway. More specifically, displacement of Eth towards values larger than the sputtering threshold indicates an inhibiting surface chemistry while displacement towards lower energy is associated to an enhancing chemistry. For CBN films etched in an inductively coupled chlorine plasma, we measured Eth ~65 eV at 1 mTorr, ~240 eV at 10 mTorr, and ~400 eV at 15 mTorr. The threshold obtained in pure Ar plasma was similar to that achieved in Cl_2 at 1 mTorr, which suggests that CBN etching at low chlorine number densities is dominated by pure physical sputtering. This is consistent with TOF-SIMS measurements that showed comparable Ca, Ba, and Nb depth profiles for the samples etched in pure Ar and in 1 mTorr, Cl_2 plasmas. At 10 mTorr, the chlorine uptake was an order of magnitude higher than at 1 mTorr. In addition, we observed an important concentration of $BaCl_x$ and $NbCl_x$, with a considerable amount of non-volatile $BaCl_2$and $NbCl_2$ closer to the topmost surface. Therefore, the higher etching threshold observed at 10 and 15 mTorr results from the formation of reaction products that are more difficult to etch than the bare CBN surface. A similar inhibiting chemistry was observed for STO films etched in a fluorinated plasma. Eth increased from ~50 eV in pure Ar to ~90 eV in a 30%SF_6-70%Ar plasma, with the desorption of SrF_x compounds being the rate-limiting step.

2:20pm **PS-TuA2 Influence of Ion Energy and Ion Flux on Polystyrene Modification by Electron Beam Generated Plasma**, ***E.H. Lock***, *S.G. Walton, R.F. Fernsler, M. Baraket*, Naval Research Laboratory

Electron beam generated plasmas constitute a unique class of plasmas due to their intrinsic low electron temperatures (< 1 eV), plasma potentials and thus ion kinetic energies. For the treatment of polymers, these plasmas have demonstrated the ability to change the surface energy and chemistry with limited change in surface topography and low etch rates. Successful increase in surface energy was achieved as a result of argon, oxygen and nitrogen treatments due to incorporation of oxygen and nitrogen functionalities. Treatment with SF_6 resulted in decrease of surface energy due to incorporation of fluorine groups. The surfaces were unchanged or even made smoother after argon and nitrogen treatments. Plasma generation in more aggressive media including oxygen and SF_6 resulted in surface roughness increase.

The dominant species driving the chemical modification process in electron beam generated plasmas differ from the ones observed in the conventional plasma sources because the high energy electron beam ionizes the gas much more efficiently and thus produces a significantly larger proportion of ions. Thus, the influence of metastables and photons is limited.

This study addresses the question of the influence of the increased kinetic energy and ion fluxes on the polymer surface modification. Ultra thin polystyrene film was chosen as a model substrate due to its well understood behavior. The changes in surface energy, chemistry, etch rates and glass transition temperatures of the polymer were investigated. The chosen gas environments are pure argon and argon/oxygen mixtures. Argon allows for studying the effects of surface activation and physical sputtering. In argon/oxygen mixtures the influence of reactive species is critical for the surface modification processes.This work was supported by the Office of Naval Research. E. H. Lock and M. Baraket appreciate the support of the National Research Council.

2:40pm **PS-TuA3 Energy Considerations in Plasma-Surface Interactions**, ***M. Goeckner***, *C.T. Nelson, SP. Sant, E.A. Joseph, B.S. Zhou, L.J. Overzet*, University of Texas at Dallas **INVITED**

Plasma processes have been used for close to four decades in the semiconductor industry and even longer in other fields. Because such process systems are complex, many individuals subdivided the complete system into three main subsystems, gas-phase chemistry, plasma physics and surface chemistry/physics. Using this methodology, considerable knowledge has been gained in fundamental processes found in the gas-phase chemistry and plasma physics. Despite numerous high quality studies, understanding the surface subsystem has proven to be challenging. In part this is due to the interactions of the three subsystems. In this paper we will examine a model of plasma-surface interactions which is based on surface-averaged quantum mechanical processes. Using the model we arrive at a general model describing both etch and deposition. We will show how energy considerations, such a local surface temperature, play major roles in such processes. We will examine in some detail the link between the model and experimental data obtained from fluorocarbon plasmas. This work is supported by a generous gift from Applied Materials.

4:00pm **PS-TuA7 Effect of Energetic Ions on Plasma Damage of SiCOH Low-k Material**, ***E. Kunnen***, *A. Urbanowicz, D. Shamiryan, H. Bender, A. Franquet, H. Struyf, W. Boullart, M.R. Baklanov*, IMEC, Belgium

In the semiconductor industry, the number of transistors per unit area has steadily increased over the past 40 years according to Moore 's Law. As a consequence, the distance between interconnecting copper lines has reached the dimensions where capacitive coupling between the lines becomes important. To reduce capacitive coupling, low-capacitive materials, so-called low-k materials, have been investigated and integrated. A lower capacitive value can be achieved by making hydrophobic porous materials from low polarizable molecules. However, during integration these materials are exposed to etch and strip plasmas, which results in a plasma damaged material with an increased k-value. In this study we want to shed light on the mechanism of how bombarding ions and chemically active radicals damage low-k materials.

As low-k, a SiOCH- based material was deposited on 300mm Si wafers, and porogen material was removed by UV curing, resulting in a 180 nm-thick layer with a porosity of 33%. Since the focus is on revealing the mechanisms and not limiting the damage, we use a pure oxygen plasma of which the damaging capabilities are well known. A transformer coupled plasma reactor, Lam Versys (r) 2300 (r), is used for exposure. This etch chamber allows a separated control of the power from the coil (top power or 'TP') on the one hand, and the power fed into the plasma through the wafer (bottom power or 'BP'). While TP results in dissociation of molecules, BP determines the bias voltage over which ions are accelerated to the wafer. Three conditions have been investigated: Bottom Power Only (BPO), Top Power Only (TPO) and Top Power and Bottom Power (T&BP), flow and pressure were kept constant. The photoresist etch rate for the different conditions was measured and the low-k wafers were exposed to the different plasma conditions using a normalized exposure time. The exposed layers were analyzed by Fourier Transformed Infrared Spectroscopy (FTIR), Water Contact Angle (WCA), Spectroscopic Ellipsometry (SE), Time Of Flight Secondary Ion Spectroscopy (TOFSIMS), Energy Filtered Transmission Electron Microscopy (EFTEM), Water and Toluene Based SE and mass measurements.

It was shown that the bombarding ions densify and seal the top layer, which makes it more difficult for the oxygen radicals to penetrate into the low-k and damage it. As a function of time, all applied conditions obey a logarithmic oxidation equation. A model that explains the equation is proposed: the oxygen radicals recombine to oxygen molecules in the damaged layer through surface reactions leading to an exponential decrease in radical concentration with depth resulting in the logarithmic time dependence.

4:20pm **PS-TuA8 193 nm Photoresist Roughening in Plasmas: VUV Photons and Synergistic Mechanisms**, ***M.J. Titus****, *D.G. Nest, D.B. Graves*, University of California, Berkeley

Plasmas can either roughen or smooth 193 nm photoresist (PR), but little is known about mechanisms or controlling variables. We report measurements of 193 nm PR roughness as a function of ion energy, substrate temperature, VUV fluence, and photon-to-ion flux ratio, in a well-diagnosed inductively coupled Ar plasma. Comparisons are made to analogous vacuum beam experiments. We seek to answer the question: what "knobs" control surface texture? We focus special attention on the role of VUV photons and their synergistic interactions with other plasma effects. Fourier transform infrared (FTIR) transmission measurements as a function of VUV photon fluence demonstrate that VUV-induced bond breaking occurs over a period of time. We present a model based on the idea that VUV photons initially deplete near-surface O-containing bonds, leading to deeper, subsequent penetration and more bond losses, until the remaining near-surface C - C bonds are able to absorb the incident radiation. Fitted model photo-absorption cross sections compare well with literature values. The model is tested and shown to be valid by comparing to measurements of VUV lamp exposures in a vacuum beam system and in the Ar ICP.

4:40pm **PS-TuA9 Electron, Ion and Vacuum Ultraviolet Photon Beam Effects in 193 nm Photoresist Roughening**, ***T.-Y. Chung***, *D.G. Nest, G.K. Choudhary, J.J. Végh, D.B. Graves,* University of California, Berkeley, *F. Weilnboeck, G.S. Oehrlein,* University of Maryland, College Park, *E.A. Hudson,* Lam Research Corp., *M. Li, D. Wang*, Dow Electronic Materials

Previous vacuum beam studies showed that PMMA-based 193 nm photoresist (PR) will roughen due to the synergistic effects of ion bombardment, vacuum ultraviolet (VUV) photon flux and substrate heating [1]. FTIR measurements show that VUV photons break C-O bonds to a depth of about 100 nm in this PR. Using the same vacuum beam apparatus, we show that electron beam exposure (energies ~ 10^3 eV) of this PR results in similar C-O bond breaking. However, the effect of e-beams on PR roughening is very different from that of VUV photons. Electron beams can either promote or inhibit roughening with simultaneous ion and VUV photon exposure, depending on electron fluence. At high electron fluence, simultaneous e-beam/VUV/ion exposure appears to suppress VUV/ion-induced roughening. By contrast, lower fluence e-beams amplify the synergistic effects of ions and VUV photons, increasing roughness. It is known from electron beam resist studies that low fluence e-beams scission PMMA, but higher electron fluences induce cross-linking [2]. We tentatively conclude that any effect that amplifies PR scissioning during ion

---

* PSTD Coburn-Winters Student Award Finalist

bombardment increases roughening, whereas any effect that induces cross-linking will suppress roughening. Finally, we discuss the nature of the dynamic changes occurring within the PR during separate and simultaneous exposures of ions, VUV photons and electrons.

[1] Nest, D., et al., Synergistic effects of vacuum ultraviolet radiation, ion bombardment, and heating in 193 nm photoresist roughening and degradation. *Applied Physics Letters*, 2008, 92(15).

[2] Hatzakis, M., Electron resists for microcircuit and mask production. *Journal of the Electrochemical Society*, 1969. 116(7): p. 1033.

5:00pm **PS-TuA10 Ion and VUV Radiation Induced Material Modifications of Advanced Photoresists During Plasma-Etching: Temporal Evolutions of Modified Surface Layers**, *F. Weilnboeck,* ***R.L. Bruce****, G.S. Oehrlein,* University of Maryland, *M. Li, D. Wang,* Dow Electronic Materials, *D.B. Graves, D.G. Nest, T.-Y. Chung,* University of California, Berkeley, *E.A. Hudson*, Lam Research Corp.

Plasma processes used for pattern transfer of nanometer structures can lead to severe material modification and roughness development of photoresist (PR) materials. We studied the temporal evolution of blanket and patterned films of fully formulated 193nm PR in Ar and Ar/C_4F_8 plasma discharges. The contribution of the optical radiation component to the overall material modification seen after direct plasma exposure was investigated by applying a filter approach which protects the PR against ion bombardment and neutral deposition. Different filter materials allow testing the influence of emission spectra and wavelength ranges of the plasma radiation from visible to vacuum ultraviolet (VUV) light. Material modifications were characterized by ellipsometry, x-ray photoelectron spectroscopy, Fourier transform infrared spectroscopy, atomic force microscopy and scanning electron microscopy. In-situ ellipsometry, employing a setup which enables separation of the optical radiation component and other plasma components, enabled to investigate in real time PR degradation effects during plasma processing. The depth dependence of PR degradation was obtained by optical multilayer ellipsometric simulations of the data.

For the plasma discharge chemistries examined, the material modifications depended strongly on PR molecular structure, exposure radiation wavelength range and plasma chemistry. Material degradation was increased for increasing photon energy, and lead to substantial oxygen loss at the PR surface and in the PR bulk. The material modification depth showed a significant dependence on the emission spectrum of the plasma discharge. The amount of oxygen lost in the material bulk was found to directly correlate with a reduction in PR film thickness. Results indicate that compared to the pure Ar discharge (main emission at 104 and 106nm) material bulk modifications are significantly higher for Ar/C_4F_8 discharges (main emission above 130nm [1]) leading to PR film thickness reduction of up to 20nm. Whereas ion bombardment modified the PR to a depth of ~ 1nm for our conditions during the first few seconds of plasma exposure and then saturated, plasma radiation modified the PR near-surface region to a depth of several tens of nm over a period of tens of seconds.

[1] Woodworth, J.R., et al., Absolute intensities of the vacuum ultraviolet spectra in oxide etch

plasma processing discharges, JVST A, 2001, 19(1)

5:20pm **PS-TuA11 Mechanism for Generation of Molecular Level Line-Edge Roughness of ArF Photoresist during Plasma Etching Processes**, ***K. Koyama****, B. Jinnai,* Tohoku University, Japan, *S. Maeda, K. Kato, A. Yasuda, H. Momose,* Mitsubishi Rayon Co., Ltd., Japan, *S. Samukawa*, Tohoku University, Japan

ArF photoresists, namely chemically amplified photoresists, have been used in recent 193-nm lithography processes. However, ArF photoresists have serious problems during plasma etching processes, such as line-edge roughness (LER). LER can be classified with pattern-size roughness, called "low-frequency LER," and molecular-level-size roughness, called "high-frequency LER". Especially, high-frequency LER is more serious problem for wiring in ULSI devices of less than 32 nm. In order to overcome these issues, it is essential to understand the relationship between irradiation species from plasma (ions, electrons, radicals, and ultraviolet/vacuum-ultraviolet (UV/VUV) photons) and molecular level reactions on the ArF photoresist surface.

In this study, we investigated the effects of UV/VUV radiation, ion bombardment and gas species on ArF photoresists by using our developed neutral-beam process. Samples were etched by Ar- or Cl_2-neutral beam and Ar- or Cl-ion and UV/VUV photon. The surface roughness of the films was measured by SPM. A comparison of neutral beam irradiation with ion and UV/VUV photon irradiation showed that surface roughness of ArF photoresist increased after ion and UV/VUV-photon irradiation for both gasses. Especially, in the case of chlorine gas, significant surface roughness is observed by adding UV/VUV photon. To investigate the effects of irradiation species on the ArF photoresist polymer structure, we analyzed the chemical bonding states in ArF photoresist polymers by using FTIR. FTIR measurement showed that the lactone and ester units in the base polymers were vulnerable to physical bombardment, chemical reactions, and UV/VUV photon irradiation. The vulnerability results in changes in base-polymer structure that could account for the differences in the etching rates and surface roughness of ArF photoresist films. Our results demonstrated that UV/VUV photon irradiation plays an important role for generation of molecular level line-edge roughness.

5:40pm **PS-TuA12 On the Absence of Post-Plasma Etch Surface and Line Edge Roughness in Vinylpyridine Resists**, ***R.L. Bruce*****, F. Weilnboeck, T. Lin, R.J. Phaneuf, G.S. Oehrlein,* University of Maryland, *W. Bell, C.G. Willson,* UT-Austin, *D.G. Nest, G.K. Choudhary, J.J. Végh, D.B. Graves,* UC-Berkeley, *A. Alizadeh*, GE Global Research

Reducing formation of line edge roughness during photoresist mask pattern transfer by plasma etching is becoming increasingly important as the critical dimensions of devices continue to shrink. We have found that using a nitrogen-containing polymer, poly(4-vinylpyridine) (P4VP), as resist completely eliminated plasma-induced surface and line edge roughening for pattern transfer process conditions that produced significant roughness in a wide variety of other polymers in Ar-containing gas discharges of various gas chemistries and over long plasma exposure times. This effect was investigated by considering the influence of the plasma species (ions, neutrals, VUV) as well as the polymer structure and comparing results with polymers that were prone to surface roughening, such as polystyrene. Material modification was characterized by in situ ellipsometry, X-ray photoelectron spectroscopy, and atomic force microscopy. Plasma-induced modifications in the polymer film are shown to cause changes in the mechanical properties at the surface leading to the development of residual stresses that creates surface roughness after plasma etching. We also investigated how nitrogen in the polymer structure as well as the gas discharge influences the mechanical stresses at the surface. Patterned films were also plasma-exposed to the same conditions and characterized by scanning electron microscope. The absence of surface roughness in P4VP is shown to eliminate LER in 3D features. Finally, we provide a comprehensive model to show how the difference in the plasma surface modification in P4VP compared to polymers such as polystyrene leads to elimination of surface roughening.

Advanced Surface Engineering
Room: C4 - Session SE+TF-TuA

Glancing Angle Deposition II
Moderator: K. Robbie, Queen's University, Canada

2:00pm **SE+TF-TuA1 Deposited Nanorod Films for Biosensor Applications**, ***W. Zhang***, University of Illinois at Urbana-Champaign, *S.M. Kim*, Chung-Ang University, Korea, *N. Ganesh,* Intel, *I. Block, P. Mathias, B.T. Cunningham*, University of Illinois at Urbana-Champaign **INVITED**

Planar photonic crystals have been used as the basis of many biological sensing devices. Here, we successfully demonstrated that the combination of the photonic crystal structures and a dielectric nanorod coating prepared by the glancing angle deposition technique can lead to significant increases in the device sensitivity.

By incorporating a TiO_2 nanorod coating onto the label-free biosensor structure, the surface area of the device is increased. The sensitivity of high surface area sensors is compared with sensors without the high surface area coating. Results for detection of polymer films, proteins, and small molecules indicate up to a seven-fold enhancement of detected adsorbed mass density.

When a TiO_2 nanorod coating is applied on top of the high index layer of an enhanced fluorescence biosensor, the emission intensity of a fluorescent dye on the device is increased by over one hundred times compared to a reference glass slide. The increased sensitivity is due to the combined effects of enhanced near-fields and enhanced surface area. The sensitivity is further increased by close to two hundred times when a TiO_2 nanorod film is used as the high index layer of the photonic crystal structure.

The planar photonic crystal is also combined with a SiO_2–Ag "post-cap" nanostructure for applications in surface-enhanced Raman spectroscopy (SERS). It is demonstrated that the resonant near fields of the photonic crystal could be used to efficiently couple light from a laser to the Ag nanoparticles to achieve a high SERS enhancement factor.

---

* PSTD Coburn-Winters Student Award Finalist

2:40pm **SE+TF-TuA3 Surface Enhanced Raman Scattering from Silver Nanorod Array Substrates: Characteristics and Origin**, ***Y. Liu***, *Z. Zhang, R.D. Dluhy, Y. Zhao*, University of Georgia

Surface-enhanced Raman scattering (SERS) has been a powerful analytical tool in chemical and biosensing applications. Silver nanorod array fabricated by oblique angle deposition can give a very strong SERS enhancement ($>10^8$). The SERS enhancement depends strongly on the length of nanorods, the incident angle of excitation light, the polarization states of excitation light, and the reflectance from substrate. A modified Greenler's model based on the reflection from a single Ag nanorod and the substrate as well as dipole radiation is proposed to explain these SERS characteristics. The theoretical calculation qualitatively agrees well with the experimental results. However, the location of the strongest SERS enhancement and the nature of such an enhancement are still unknown. To answer this question, we have designed another set of experiments, by taking the advantage of oblique angle deposition, to put Raman probe molecules on different locations of Ag nanorod array substrates and found that the apparent SERS enhancement factor is about 50 ~ 200 times from the surface of the nanorods than that from the Ag thin film surface under Ag nanorods array. These effects cannot be interpreted directly by the local electric field enhancement effect. By combining the local electric field effect calculated by three dimensional finite-difference time-domain method and the anisotropic optical absorbance of the SERS signal from the anisotropic Ag nanorod array, the numerical calculations are semi-quantitatively agree with the experimental results.

* This work is supported by National Science Foundation (NO. ECS-0701787) and US Army Research Laboratory (W911NF-07-2-0065).

References:

Y. -J. Liu, J. -G. Fan, Y. -P. Zhao, S. Shanmukh, and R. A. Dluhy, *Angle Dependent Surface Enhanced Raman Scattering Obtained from a Ag Nanorod Array Substrates*, Appl. Phys. Lett. 89, 173134 (2006)

J. D. Driskell, S. Shanmukh, Y. -J. Liu, S. B. Chaney, X. J. Tang, Y. -P. Zhao, and R. A. Dluhy, *The Use of Aligned Silver Nanorod Arrays Prepared by Oblique Angle Deposition as Surface Enhanced Raman Scattering Substrates*, J. Phys. Chem. C 112, 895 (2008)

Y. -J. Liu, Y. -P. Zhao, *Simple Model for Surface-enhanced Raman Scattering from Tilted Silver Nanorod Array Substrates*, Phys. Rev. B 78, 075436 (2008)

Y.-J. Liu, Z.-Y. Zhang, Q. Zhao, R. A. Dluhy, and Y.-P. Zhao, *The Surface Enhanced Raman Scattering from Ag Nanorod Array Substrate: the Site Dependent enhancement and Layer Absorbance Effect*, J. Phys. Chem. C, in press (2009)

3:00pm **SE+TF-TuA4 Local Plasmon Resonators Combinatorially-Multilayered by Oblique Angle Deposition Technique**, ***M. Suzuki***, *R. Tabuchi, Y. Imai, S. Li, K. Nakajima, K. Kimura,* Kyoto University, Japan*, T. Fukuoka*, Archilys RP, Japan

We have successfully prepared multilayered sculptured thin films with various combinations of the layer thicknesses using a shutter system specially designed for the oblique angle deposition. A series of different thicknesses were realized on a single substrate by moving a step-shaped shutter incrementally across the sample during the oblique angle deposition, while an ordinary straight shutter was used during normal deposition. This deposition process has been applied to fabricate local plasmon resonators comprised of the sandwich of Au nanorod array (NRA)/structured dielectric layer/Ag mirror. The fundamental optical properties of the local plasmon resonators have been already reported [1]. Briefly, the reflectance in NIR region can be controlled between 10^{-4} and 1 due to the strong interference. At low reflectance conditions, Au nanorods absorb most of the incident light and are expected to enhance the local electric field in their close vicinity. However, detailed relation between the optical properties of the local plasmon resonators and the combination of the thicknesses of Au and dielectric layers has never been clarified. In this study, we prepared 4x6 arrays of the local plasmon resonators which have four and six different thicknesses of Au and the dielectric layers, respectively, on a single substrate of 50x50 mm^2. The surface enhanced Raman scattering intensity measured on the element with low reflectance is about 50 times stronger than that on the Au NRA prepared on the glass substrate (without Ag mirror). This indicates that the local electric field in the NIR region is controllable by using interference. Therefore, the NRA fabricated on the mirror with appropriate spacer layers is useful not only for improving conventional biochemical sensing but also for the novel applications using spatiotemporal control of the local plasmons. For optimization of the multilayered sculptured thin films, the combinatorial approach is quite useful.

[1] M. Suzuki et al., Journal of Nanophotonics **3**, 031502 (2009).

4:00pm **SE+TF-TuA7 Influence of Substrate Temperature on Glancing Angle Deposited Ag Nanorods**, ***C. Khare****, C. Patzig, J.W. Gerlach,* Leibniz-Institut of Surface Modification, Germany*, B. Fuhrmann,* Martin-Luther-University Halle, Germany*, B. Rauschenbach*, Leibniz-Institut of Surface Modification, Germany

When Ag sculptured thin films (STFs) were grown with glancing angle deposition by ion beam sputtering at either room temperature or elevated substrate temperatures T_S, an enormous topographical difference could be observed. The incident particle flux reached the silicon substrate at a glancing angle $\beta \geq 80°$ as measured to the substrate normal . A slit aperture was used in order to reduce the particle beam divergence. At room temperature, columnar structures were formed, irrespective of the presence of the slit aperture. At elevated temperatures (300° C, 350° C) and collimated particle flux in the presence of the slit aperture, however, accelerated surface diffusion causes the growth of nanorod- and nanowire-like structures. In the absence of the slit aperture, the flux beam divergence is higher, leading to island- and mountain-like crystalline structures that were found at elevated temperatures. The density of the nanorods and nanowires was observed to be higher on the planar Si substrates in comparison to honeycomb-like pre-patterned substrates with different pattern periods. On the patterned substrates, the nanorods are not necessarily found to be evolving on the seed points, but can rather also be observed in intermediate pre-pattern spaces. The glancing angle deposited films were observed to be polycrystalline, where the (111) crystal orientation of the film is dominant, while the presence of the less intense (200) reflection was noticed from XRD measurements. In contrast, the closed films deposited with $\beta \approx 0°$ at high temperatures were found to be epitaxial with (200) orientation.

4:20pm **SE+TF-TuA8 Temperature Driven Anomalous Scaling during Glancing Angle Deposition**, ***S. Mukherjee****, D. Gall*, Rensselaer Polytechnic Institute

Ta, Nb, Cr and Al nanorod structures were grown by glancing angle physical vapor deposition on a continuously rotated Si(001) substrate at an incidence angle of 84° and at substrate temperatures T_s = 300-1125 K. The width w of the self-affine nanorods increases with the height h according to $w\alpha h^p$. The growth exponent p is a function of the homologous substrate temperature θ, which is the ratio of T_s to the melting point T_m. All studied metallic systems exhibit the same $p(\theta)$ curve: p approaches a value of 0.5 for negligible surface diffusion ($\theta < 0.1$) and monotonously decreases to p = 0.39 for θ = 0.2, as predicted by Meakin and Krug's model of nanorod growth with limited surface diffusion and by Mullins-Herring's model of 2+1 dimensional interface growth, respectively. However, p increases dramatically for θ = 0.22-0.26, to reach an anomalous value of 0.71. Above the transition temperature $\theta_c = 0.24\pm0.02$, the growth exponent decreases to reach p = 0.3 at θ = 0.42.

We present a semi-analytical model using mean-field nucleation and non-linear chaos theory that relates p with the exponential divergence λ from a surface diffusion limited material independent morphology that is controlled by atomic shadowing. p is a function of the average island separation distance $<s>$, which is a measure of the diffusion length scale and varies with θ, the activation energy E_m for surface diffusion, the critical island size i, and the dimensionality of adatom surface diffusion. The model predicts a transition from a 2-d to a 3-d island growth mode at θ_c. This transition, in turn, exacerbates the chaotic bifurcation associated with the atomic shadowing by the islands on the nanorod growth fronts, resulting in the higher growth exponents above θ_c. The model also provides a single homologous activation energy E_m/kT_m = 2.46 for surface diffusion on curved nanorod growth fronts, applicable to all studied metallic systems at all temperatures. p follows a linear function with $<s>$, in both high and low temperature regimes and the slope correlates with the slope of λ vs $\ln(h)$, indicating that the growth exponent and hence the morphology is intricately related to both shadowing and surface diffusion.

4:40pm **SE+TF-TuA9 Investigation of Surface Sensitivity of Relative Humidity Sensors through ALD Coated GLAD**, ***M.T. Taschuk***, University of Alberta, Canada*, K.D. Harris, J.M. Buriak, M.J. Brett*, NRC National Institute for Nanotechnology, Canada

We have been investigating the performance and optimization of nanostructured relative humidity (RH) sensors produced by glancing angle deposition (GLAD) [1 – 2]. GLAD offers significant advantages for sensor applications, including extremely large surface areas, response times as low as 50 ms, and the use of any material compatible with physical vapour deposition. However, there remain a number of open questions regarding the underlying physics of GLAD RH sensor performance and response time. Response time and magnitude varies with the size and nature of pores in our sensors, and the interaction between the analyte and deposited material. To better understand the analyte-surface interactions, we have studied the performance of RH sensors with a thin coating of TiO_2 deposited by atomic-layer deposition (ALD).

Columnar thin films of Si and TiO_2 were produced by GLAD on interdigitated electrode substrates, creating a RH sensor. The GLAD sensing layer was conformally coated with TiO2 films by atomic layer deposition. In this process, the deposition chamber is evacuated and the reactive precursor, titanium isopropoxide (TIPO), is admitted. A thin layer of TIPO saturates the exposed substrate surfaces, and once complete, the deposition chamber is purged and oxygen is introduced. At the precursor-loaded substrate, this oxygen reacts with TIPO in a plasma-driven process to produce a thin layer of TiO_2 conformally surrounding the high surface area GLAD film. In this work, the ALD process is repeated cyclically to build up TiO_2 layers of different thicknesses.

Preliminary investigations have used 1.5 µm Si and TiO_2 GLAD films, coated with ALD TiO2 films between 2 nm and 32 nm thick. The RH sensing properties of these devices were testing using a custom environmental chamber [1]. As expected, the uncoated Si and TiO_2 thins films exhibited different responsivities. However, once the different sensors were coated with ALD TiO2 layers as thin as 2 nm, sensor response was very similar, indicating that sensor function is dominated by surface properties. To better investigate the transition between the GLAD post dominated response and ALD-layer dominated response, a series of films with thinner ALD coatings is underway. The sensor response will be characterized as a function of RH, electrical probe frequency, and ALD layer thickness. Current experimental results will be presented.

[1] J.J. Steele et al. IEEE Sensors Journal (2008) Vol 8. pp. 1422 - 1429

[2] M.T. Taschuk et al. Sensors and Actuators B (2008) Vol. 134, pp. 666 - 671.

5:00pm **SE+TF-TuA10 Direct Measurement of Porosity in Glancing Angle Deposited Thin Films**, *A.R. Gonzalez-Elipe,* ICMSE (CSIC - U. Seville), Spain, ***F. Yubero***, CSIC, Spain, *J.R. Sanchez-Valencia*, ICMSE (CSIC - U. Seville), Spain

Porosity of thin films is generally estimated in an indirect way by looking to their refraction index. In the present communication we determine directly the porosity of the a series of glancing angle deposited films by measuring the adsorption/desorption of water as a function of the partial pressure of water vapour in contact with the film. The method consists of measuring the changes in the vibration frequency of a quartz crystal monitor (QCM) with its surface covered by the thin films.1 The analysis of the obtained curves permits to estimate the total porosity of the films, its partition between mesopores (pores larger than 2 nm) and micropores (pores smaller than 2 nm) and the pore size distribution function. Results are shown for a series of titanium oxide thin films prepared by evaporation at different glancing angles between 60º and 90º. It is shown that both the total porosity and the partition between meso and micropores change with the evaporation angle. A good correlation exists between these measurements and the optical constants of these films determined by ellipsometry. Analysis of the films by Scanning Electron Microscopy (SEM), and Atomic Force Microscopy (AFM) gives some hints to account for the evolution of porosity as a function of the evaporation angle.

1) A. Borrás, J.R. Sánchez-Valencia, J. Garrido-Molinero, A. Barranco, A.R. González-Elipe, Microporous and Mesoporous Materials 118 (2009) 314-324

5:20pm **SE+TF-TuA11 Monoclinic Magnetic Anisotropy and Hybridization of GLAD Sculptured Thin Films**, *A. Kjerstad, D. Schmidt, T. Hofman,* ***M. Schubert****, E. Schubert, R. Skomski, D. Sellmeyer*, University of Nebraska - Lincoln

We report on the magnetic monoclinic anisotropy behavior of cobalt sculptured GLAD structures. Exciting new physics are presented in a model showing the nanostructures result in a thin film with tunable properties dependent on orientation, tilt, and patterning of the slanted nanowires. These sculptured thin films can be further modified – non-magnetic structures are coated with ferroelectric polymers for novel surfaces. Alternatively, magnetic structures are modified using non-magnetic materials, once again creating hybridized structures with undiscovered properties.

Surface Science
Room: C1 - Session SS1+PS+TF+AS+NS-TuA

Non-Thermal Chemistry / Ion, Electron Processes
Moderator: A.V. Walker, University of Texas at Dallas

2:00pm **SS1+PS+TF+AS+NS-TuA1 Growth and Purification of Nanostructures Deposited by Electron Beam Irradiation: A Surface Science Perspective*****, H. Fairbrother****, J. Wnuk, J. Gorham, S. Rosenberg,* Johns Hopkins University*, T. Madey,* Rutgers*, W.F. van Dorp, K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam induced processing (FEBIP) of volatile organometallic precursors has emerged as an effective and versatile method of fabricating metal-containing nanostructures. However, to improve the materials properties of FEBIP nanostructures, provide information that can aid in the rational design of new precursors and improve the modeling of the FEBIP process it is necessary to better understand the molecular level processes associated with the electron stimulated decomposition of organometallic precursors. To address this issue, we have employed a UHV-surface science approach to study the electron induced reactions of dimethyl(acetylacetonate) gold(III) (Au(acac)Me_2), a common precursor used for Au deposition in FEBIP, adsorbed on solid substrates. Surface reactions, reaction kinetics and gas phase products were studied using incident electrons in the energy regime between 40-1500 eV, using a combination of XPS, RAIRS and MS. XPS data indicate that electron irradiation of Au^{III}(acac)Me_2 is accompanied by the reduction of Au^{III} to a metallic Au^0 species embedded in a carbon matrix while MS reveals the concomitant evolution of methane, ethane and hydrogen. The electron stimulated decomposition of the Au^{III}(acac)Me_2 precursor can be described by a first-order decay process with respect to the surface coverage, with a rate constant that is proportional to the electron flux and a total reaction cross-section of ≈3.6 x 10^{-16} cm^2 at an incident electron energy of 520 eV. As a function of the incident electron energy, the maximum deposition yield was observed at ≈175 eV. Our results are consistent with the idea that those carbon atoms removed as volatile species from the Au^{III}(acac)Me_2 precursor during FEBIP are associated with methyl groups attached to the central Au atom. In related studies we also studied the effects of atomic oxygen and atomic hydrogen on Au-containing carbonaceous films deposited by electron beam irradiation of Au(acac)Me_2, as a potential route to purify FEBIP deposits. Atomic oxygen was found to be the more effective of the two radical treatments in removing carbon, although a surface layer of gold oxide was formed. Subsequent exposure of this overlayer to atomic hydrogen rapidly removed the oxide, resulting in a pure Au film. AFM analysis of FEBIP deposits before and after radical treatment support the idea that carbon abatement is accompanied by a decrease in particle size.

2:20pm **SS1+PS+TF+AS+NS-TuA2 Surface Morphology Control and 3D Structure Development with Cryogenic Assisted Electron Beam-Induced-Deposition**, ***M. Bresin****, K.A. Dunn*, University at Albany SUNY

Electron beam-induced-deposition (EBID) of platinum-containing materials was performed at cryogenic temperatures. Deposit morphology, microstructure and nanostructure have been characterized by scanning and transmission electron microscopy (SEM and TEM), and shown to be controllable by the electron fluence used for EBID. 3D structures were developed using a multilayer deposition method, facilitating the creation of hanging, suspended or incorporated-gap structures.

Experiments were performed using an FEI Nova 600 Nanolab dual beam system with a LN2 cryogenic stage, enabling substrate temperatures of -155±5oC. A gaseous platinum precursor (MeCpPtMe3) was first condensed onto the cooled substrate using a capillary-style gas injection system (GIS). Condensate thicknesses between 100nm-3mm were produced by adjusting the GIS-substrate gap and precursor crucible temperature. Next, gas flow was terminated and the condensate was irradiated with an electron beam to induce precursor decomposition. When the substrate was returned to room temperature, any unreacted precursor desorbed and was removed by the pumping system, while irradiated regions showed clear evidence of successful deposition. The morphology of the deposited material depended on exact deposition conditions, and exhibited several distinct types absent from deposits made by conventional (room temperature) EBID.

3D structures were developed with a multilayer deposition method. In this method, multiple layers were used to take advantage of the electron penetration depth within the condensate, through which the depth of deposition could be controlled. An initial layer was first condensed and a region was deposited with the electron beam to act as a substrate-anchoring site. A second condensed layer was then applied such that electrons could only penetrate to the top of the initial condensed layer. The electron beam was then shifted, to deposit a section partially over the anchoring region (in the initial layer) with the remainder over unreacted area. After reheating, part of the second deposit was found to have adhered to the anchoring region, while the rest hung over vacuum. Using similar process, structures were also developed to create embedded gaps or tunnels.

Taken together, these observations have important implications for the creation of arbitrarily large or complex structures previously untenable by EBID fabrication. The growth mechanism and potential applications will be discussed, from nanotechnology to osteointegration.

2:40pm **SS1+PS+TF+AS+NS-TuA3 Nanoscale Patterning and Graphene Film Deposition on Si using Low-energy Electron Beams**, ***T.M. Orlando****, D. Sokolov, D. Oh, K. Shepperd*, Georgia Institute of Technology **INVITED**

The physics and chemistry associated with desorption induced by electronic transitions, particularly electron stimulated desorption (ESD), is the basis for many electron-beam induced processes in materials growth, etching, and lithography. We have demonstrated experimentally and theoretically that the total ESD yield of adsorbates can be a function of the incident low-energy electron-beam direction. We refer to this phenomena as Diffraction in Electron Stimulated Desorption (DESD). We have also explored three graphene growth strategies which utilize low-energy electron beams and non-thermal reactions. The first uses electron beam irradiation in conjunction with chemical vapor deposition techniques to grow graphene directly on Si substrates. This approach utilizes unsaturated hydrocarbon precursor molecules and can be carried out at relatively low temperatures. The second involves electron-stimulated removal of oxygen and organic fragments from graphene-oxide flakes positioned on patterned Si substrates. This may allow for damage-free reduction of graphene-oxide to graphene. The third involves electron-beam removal of defects from graphene expitaxially grown from SiC(0001) substrates.

4:00pm **SS1+PS+TF+AS+NS-TuA7 A Study of the Nucleation of Focused Electron Beam Induced Deposits: Growth Behavior on the Nanometer Scale**, ***W.F. van Dorp***, Delft University of Technology, The Netherlands*, J.B. Wagner, T.W. Hansen, R.E. Dunin-Borkowski,* Danish Technical University, Denmark*, K. Hagen*, Delft University of Technology, The Netherlands

Focused electron beam-induced deposition (FEBID) 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. Currently, the highest resolution that is reported is 0.7 nm [1] using the precursor $W(CO)_6$. At this scale, deposits contain no more than a few molecules on average. Our ultimate goal is to develop the ability to deposit single precursor molecules in a consistent manner.

We perform our FEBID experiments in environmental scanning transmission electron microscopes (E-STEM) with a beam energy of 200 keV and a 0.2 nm probe. The annular dark field (ADF) signal is used for the imaging of the deposits. By recording the ADF signal during deposit growth we are able to monitor the growth process in situ. Thin, electron transparent graphite is used as a substrate and typical precursor gas pressures at the sample during the deposition were 10^{-3} to 10^{-5} Torr.

In the present study we used $Me_3PtMeCp$, a Pt-precursor that is often used in FEBID experiments [2]. To improve on the currently achieved resolution, it is important to study the nucleation stage of deposits. When using a graphite substrate we found that there is a significance difference in deposition behavior between the $W(CO)_6$ and $Me_3PtMeCp$ precursors. Where the typical growth behavior for $W(CO)_6$ is to form nm-sized or even sub-nm sized deposits, the deposits fabricated from $Me_3PtMeCp$ are a few nanometers in diameter and consist of individual sub-nm sized grains. We report on our study of this difference in growth behavior and strategies to increase the writing resolution.

[1] W.F. van Dorp, C.W. Hagen, P.A. Crozier, P. Kruit, Nanotechnology 19 (2008) 225305

[2] A. Botman, M. Hesselberth, J.J.L. Mulders, Microelectron Eng 85 (2008) 1139

4:20pm **SS1+PS+TF+AS+NS-TuA8 Direct Local Deposition of High-Purity Pt Nanostructures by Combining EBID and ALD**, ***A.J.M. Mackus***, Eindhoven University of Technology, the Netherlands*, H.J.J.L. Mulders, A.F. de Jong,* FEI Electron Optics, the Netherlands*, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, the Netherlands

Due to its ability to directly deposit nanostructures with sub-10 nm lateral dimensions electron beam induced deposition (EBID) has the potential to become a key nanomanufacturing technology. The technique suffers however from incomplete decomposition of the precursor gas and consequently a low material purity. Platinum EBID yields typically only a purity of ~15 at.% and a resistivity value orders of magnitude higher than bulk resistivity which reduces the functionality of the material for most nanoprototyping applications such as adding electrical contacts to nanodevices. In this contribution we propose a novel approach for the fabrication of high-purity Pt nanostructures based on a combination of the patterning capability of EBID and the high material quality obtained by atomic layer deposition (ALD). The latter technique yields submonolayer control of the film thickness and in the case of Pt ALD high purity (~100%), low resistivity (13±1 μΩcm) films [1]. The developed approach comprises seed layer deposition by EBID and area-selective ALD growth. For specific conditions the thermal ALD process of Pt ($MeCpPtMe_3$ precursor, O_2 gas) was found to start selectively on an EBID seed layer with a thickness equivalent to one monolayer Pt. It was established that the deposits have a uniform thickness and a high purity value (>93%), whereas the method has the potential to achieve sub-10 nm lateral dimensions. In addition to the approach and the material properties the underlying reaction mechanism of the (area-selective) Pt ALD process will be discussed, including aspects such as the role of dissociative chemisorption of O_2 molecules on Pt and the formation of H_2O, CO_2, and CH_4, reaction products.

[1] H.C.M. Knoops, A.J.M. Mackus, M.E. Donders, M.C.M. van de Sanden, P.H.L. Notten, and W.M.M. Kessels, *Electrochem. Solid-Sate Lett.* **12**, G34 (2009)

4:40pm **SS1+PS+TF+AS+NS-TuA9 Anionic Surface Processes Induced by Low-Energy Electrons**, ***P.A. Rowntree***, University of Guelph, Canada **INVITED**

The historical development of surface chemistry has largely been based on the use of free-energy-driven processes; an enormous volume of literature exists that details the search for chemical control over these processes using the classical parameters of temperature, surface composition and reagents. However, as the interest in controlling the processes grows, and the need to produce structurally resolved reactive systems increases, alternative non-thermal mechanisms are increasingly being explored in order to drive the interfacial processes into reaction channels chosen by the needs of the operator instead of the principles of thermochemistry. Our specific interest is in the control of surface processes using low-energy electrons as specialty 'reagents' that can be delivered to surfaces in a highly controlled manner, and interact with surface species according to understandable and reproducible mechanisms. The overall goal is to understand and manipulate these mechanisms to selectively interact with target molecules of our choosing to modify surfaces according to our needs.

This presentation will focus on two aspects of this 'manipulative' approach to surface chemistry. The first is our recent development of ways to selectively control where incident electrons interact with the organic monolayers that are deposited on Au(111) surfaces. These chemically homogeneous monolayers have a highly uniform electronic structure along the length of the chains, such that it is normally not possible to strongly enhance the dissociation probabilities at any given site. We have found that it is possible to selectively enhance the rupture of C-H bonds at the methyl terminations of these films by coupling the incident electron flux with anionic excitonic states of rare gas solids that are adsorbed on these methyl terminations. The energy+charge transfer process that leads to bond rupture is extremely sensitive to the incident energy as well as the chemical nature of the target species, thus enhancing the selectivity of the local modifications to the organic surface. A second set of processes will be discussed that involves the electron-induced decarbonylation of metal carbonyls adsorbed on organic surfaces to produce atomic metal deposits. We have shown that low-energy electrons can induce surface polymerization reactions in $Fe(CO)_5$ films that lead to apparent CO-elimination cross-sections greater than 1 nm^2. This strong coupling to dissociative processes allows us to develop thin metal overlayers without the substrate damage that is usually associated with using thermal evaporation or sputtering processes.

5:20pm **SS1+PS+TF+AS+NS-TuA11 Condensed Phase Electron-Stimulated Reactions: Desorbed Anions and Retained Radicals**, ***Y. Shyur***, *J. Wang, S. Lau, E. Krupczak, C. Arumainayagam*, Wellesley College

Studies of low-energy electron-induced processes in nanoscale thin films serve to elucidate the pivotal role that low-energy electron-induced reactions play in high-energy radiation-induced chemical reactions in condensed matter. While electron-stimulated desorption (ESD) experiments conducted during irradiation have yielded vital information relevant to primary or initial electron-induced processes, analyzing the products following low-energy electron irradiation can provide new insights into radiation chemistry. We have used post-irradiation temperature-programmed desorption to identify labile radiolysis products as demonstrated by the first identification of methoxymethanol as a reaction product of methanol (CH_3OH) radiolysis. Although low-energy electron-induced oligomerization reactions have been previously reported for molecules such as thiophene and cyclopropane, our electon-induced studies of CCl_4 represent the first study to specifically identify the products of such reactions, demonstrating the utility of post–irradiation temperature programmed desorption experiments to study the radiation chemistry of condensed matter. Results of post-irradiation studies have been used not only to determine the identity of radiolysis products, but also to determine the dynamics of electron-induced reactions. By comparing our post-irradiation results to previous electron stimulated desorption studies of anion production during irradiation of condensed CF_2Cl_2 and CF_3I, we examine the relationship between desorbed anions and retained radicals during dissociative electron attachment in the condensed phase.

5:40pm **SS1+PS+TF+AS+NS-TuA12 Cluster-induced Desorption and Ionization of Biomolecules for Application in Mass Spectrometry**, ***M. Dürr***, Hochschule Esslingen, Germany, *C. Gebhardt, A. Tomsic, H. Schröder, K. Kompa*, MPI für Quantenoptik, Germany

Mass spectrometry of biological macromolecules has developed into a key technology for fast routine analysis in biotechnology. A critical issue is the efficient transfer of non-volatile biomolecules out of their sample solution into the gas phase in combination with their concomitant ionization. Here we show that a beam of neutral molecular clusters consisting of 10^3 to 10^4 SO_2 molecules can be used for the desorption and ionization of biomolecules. Cluster impact on arbitrary surfaces pre-treated with biomolecules efficiently creates cold, desolvated, gas phase biomolecular ions as large as 6000 u without any need for preparation of the biomolecules in a special matrix or post-ionization after desorption. Since the cluster provides not only the energy for the desorption process but also a transient matrix during the process, the molecules are found to be desorbed without any fragmentation.

As revealed by means of molecular dynamics simulations, high kinetic temperatures in the order of a few thousand Kelvin are reached during cluster impact on the surface. However, these extreme conditions prevail only for some picoseconds, since shattering of the initial cluster leads to very fast energy dissipation. Already after 20 ps, the SO_2 cluster fragments have reached a temperature colder than the original temperature of the adsorbates. This fast energy dissipation excludes efficient energy transfer into the vibrational degrees of freedom relevant for the cleavage of the relatively large biomolecules and thus allows for their soft, fragmentation-free desorption.

Surface Science
Room: M - Session SS2-TuA

Wide Band Gap Semiconductors
Moderator: V. Bermudez, Naval Research Laboratory

2:00pm **SS2-TuA1 The Functionalization of Semiconductor Surfaces with Hemin**, ***M. Losurdo***, IMIP-CNR, Italy, *S.D. Wolter,* Duke University, *M. Giangregorio,* IMIP-CNR, Italy, *T.H. Kim,* Duke University, *G.V. Bianco, P. Capezzuto, G. Bruno,* IMIP-CNR, Italy, *A.S. Brown*, Duke University

Selective and sensitive detection of Nitric Oxide (NO) with a device that will monitor its concentration continuously for biological, environmental, and defense applications is highly desirable. One method of accomplishing this detection, is to functionalize a semiconductor surface with metaloporphyrin groups Specific metaloporphyrins may be chosen for analyte selectivity. Heme, Fe-Protoporphyrin IX (hemin), for example, binds NO with much greater affinity, than to other gases such as O2 and CO.

Herein, we present and discuss the semiconductor surface and interface chemistry involved in the chemisorption of hemin on III-V surfaces including InP, GaAs, GaN and on group-IV semiconductors including SiC and Si.

The peculiarity of our study is the use of spectroscopic ellipsometry for the monitoring of surface coverage and interface phenomena. Ellipsometry data are corroborated by X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM) and electrical force microscopy. We discuss the dependence of semiconductor surface treatments e.g. native oxide, chemical treatments, passivating processes whose role is pre-conditioning the surface with –H or –NH terminal groups) on the self-assembling of the functionalizing biomolecules, and of the concentration of the hemin solution and chemistry duration on the chemistry and kinetics of the various semiconductor functionalization. We report also on the effect of benzoic acid addition to the hemin solution as a spacer to prevent formation of hemin aggregates in favor of normal-to-surface hemin orientation. By investigating a number of semiconductor base systems with a gap ranging in a broad range from 0.4 eV (InAs) to 3.4 eV (GaN) we demonstrate for the first time the correlation existing between the sensing activity and the semiconductor gap. This correlation might be useful to choose the appropriate semiconductor-based platform for a target sensing application. A correlation between the band gap of the semiconductors, the surface binding sites and the efficacy of functionalization is established and discussed. .

This work is supported by the 7FP European Project NanoCharM (Multifunctional NanoMaterial Characterization exploiting ellipsometry and polarimetry)

2:20pm **SS2-TuA2 Photoelectrochemical Etching of a Non-Polar GaN LED**, ***H.-Y. Kim***, Korea University, South Korea, *M.A. Mastro, C.R. Eddy, Jr.*, US Naval Research Laboratory, *J. Kim*, Korea University, South Korea

Light emtting diode (LED) strucutres fabricated from GaN-based material grown from along the polar c-axis posses a large polarization field within the active quantum well that hampers the efficiency of the device. This internal electric field separates the electrons and holes, which reduces the recombination rate in the quantum well (QW). To improve the light emission efficiency, we fabricated QW-LEDs from GaN-based material grown in the non-polar a-plane on r-plane sapphire. Implementing this approach to enhance the internal quantum efficiency on commerically available 2-inch r-plane sapphire required the development of a medium temperature AlN/GaN buffer layer scheme. Not only improved internal efficiency but also improved external efficiency is required to achieve high brightness LEDs. To date, the only widely applied technique to enhance the extraction of light from commercial polar GaN LEDs is to roughen the surface by dry or wet etching. We developed a photoelectrochemical (PEC) etching approach for the a-plane non-polar GaN LED. The samples were dipped into the KOH solution and exposed to UV light generated from a mercury lamp. A detailed invetigation was conducted into the effect KOH concentration as well as the intenisty of UV exposure on the etch rate and morphology of the surface. The PEC etching of the assymertic bond structure along the [0001] and [1-100] directions generated the elongated dimples and roof-shape pillars. The denisty of the pillars and the width of the dimples increased with increased etching time. The dimples and pillars (surface texturing) on the surface provides an ensemble of angles for light to escape that is normally trapped within the crystal. Photoluminescence measurements were conducted to investigate the relationship between extration efficiency and surface texturing by this PEC etching technique.

2:40pm **SS2-TuA3 Surface Photovoltage and Band Bending in GaN**, ***A.A. Baski***, *M.A. Foussekis, M.A. Reshchikov*, Virginia Commonwealth University **INVITED**

Although GaN is a wide-band gap semiconductor being successfully utilized in high-temperature and optoelectronic devices, the influence of surface effects such as band bending on the electrical and optical properties of GaN is not yet well understood. It is known that negative surface charge on air-exposed, undoped *n*-type GaN causes a substantial upward band bending of 0.4 – 1.5 eV. This band bending can be reduced by 0.3 to 0.9 eV during UV illumination, known as surface photovoltage (SPV), due to the accumulation of photo-generated holes at the surface. We have investigated the dependence of the SPV on illumination intensity and wavelength, as well as its transients after turning on and off illumination, using a Kelvin probe mounted in an optical cryostat. As expected, the initial SPV rise is slow at low illumination intensities and fast at higher intensities, where its initial slope is a linear function of illumination intensity. The SPV signal in air ambient under UV illumination increases within seconds to a maximum (0.4 to 0.7 V), but then gradually decreases during illumination. A similar behavior occurs in an oxygen environment (but not nitrogen), indicating that surface oxygen species are the primary component responsible for the observed SPV decrease. In vacuum, the SPV signal quickly increases but then slowly increases under UV illumination. This SPV behavior is consistent with the photo-induced adsorption of negatively charged oxygen species in air and their desorption in vacuum. After ceasing illumination, the SPV decays nearly logarithmically regardless of environment, but requires substantially longer to reach its dark value after extended illumination in vacuum.

We explain the transient and steady-state SPV under UV illumination using both internal and external mechanisms. The internal mechanism involves photogenerated holes that accumulate at surface states and recombine with free electrons from the bulk, whereas the external mechanism involves electrons that tunnel through a thin oxide layer and are captured by surface species, resulting in chemisorption. Our proposed phenomenological model quantitatively explains SPV data for low intensity UV light using only the internal mechanism; however, illumination at high intensities requires the inclusion of photo-induced chemisorption or desorption processes. Our studies to date have focused on n-type GaN, but we have preliminary data for p-type GaN indicating an initial downward band bending of ~1 eV and an unexpected increase in band bending under UV illumination. Studies of the band bending and SPV transients in different ambients are in progress and will be reported as well.

4:00pm **SS2-TuA7 Adsorption Processes on Silicon Carbide Surfaces**, ***J. Pollmann***, Universitaet Muenster, Germany **INVITED**

Many experimental and theoretical studies of adsorption processes on semiconductors have employed Si(001) as a prototype substrate surface. The ionic group IV compound semiconductor silicon carbide (SiC), which is of large fundamental interest and of high application potential for electronic devices and sensors, offers particularly interesting new degrees of freedom for adsorption because of its different lattice constant and its rich variety of surface reconstructions giving rise to very amazing adsorption behaviour. For example, molecular hydrogen adsorbs dissociatively on SiC(001)-c(4x2) while it does not adsorb on SiC(001)-(3x2) at room temperature although both surfaces are characterized by similar surface dimers. Likewise the covalent attachment of organic layers to the SiC(001)-(3x2) surface, contrary to the Si(001)-(2x1) surface, gives rise to structurally well-defined configurations that can play a key role in organic functionalization. Incorporating new functionalities at SiC surfaces by adsorption of hydrogen or hydrocarbons requires a detailed understanding of the adsorbate-surface structure and its properties. In this talk adsorption of hydrogen, acetylene, ethylene and benzene on SiC(001) surfaces will be discussed. Scrutinizing a number of conceivable reaction scenarios within first-principles theory allows us to follow surface reactions on a microscopic level giving access to reaction mechanisms, transition states, barrier heights and adsorption energies and thus to identify the physical origin and nature of the peculiar adsorption behavior of SiC(001) surfaces. The theoretical results will be reviewed and discussed in comparison with available experimental data, as well as results for related adsorption processes on the Si(001)-(2x1) surface.

5:00pm **SS2-TuA10 Temperature Stabilised Surface Reconstructions in Humid Atmospheres and pH-dependent Stabilization Mechanism at Polar ZnO(0001) –Zn Surfaces**, ***M. Valtiner***, *M. Todorova, J. Neugebauer*, Max-Planck-Institute für Eisenforschung GmbH, Germany, *G. Grundmeier*, University of Paderborn, Germany

The surface chemistry of oxides in humid atmospheres and in water based electrolytes (as e.g. oxide dissolution promoting effects of H+ and OH-) is an important aspect of molecular adhesion and related phenomena. Preparation and characterization of atomically well-defined oxide/electrolyte model interfaces, which allow well-defined molecular adhesion studies, are the most challenging issue in this context. Therefore, this contribution will focus of experimental results of the preparation of single crystalline ZnO(0001)-Zn model surfaces in humid atmospheres and complementary DFT-based ab-initio thermodynamics studies.

The main focus is the preparation and characterisation of surfaces, which are well defined on an atomic scale. The atomic structure of the polar ZnO(0001) surfaces in dry and humid oxygen environment was studied by diffraction experiments and density-functional theory in combination with atomistic thermodynamics. Our results indicate that for similar stoichiometries a large number of very different, but energetically almost degenerate reconstructions exist. Thus vibrational entropy, which could be safely neglected for most semi-conductor surfaces, becomes dominant giving rise to a hitherto not reported strong dependence of surface phase diagrams on temperature. Based on this insight we are able to consistently describe and explain the experimentally observed surface structures on polar ZnO(0001) surfaces [1,2].

Moreover, it will be shown that ZnO(0001)-Zn surfaces are stable and single crystalline within a wide pH range. An in-situ AFM study of the acidic dissolution allowed an nanoscale imaging of the dissolution process and hence a mechanistic understanding of the dissolution process of ZnO can be supported on a nanoscopic level [3]. Finally, first results of combining single molecule adhesion measurements with these single crystalline substrates will be highlighted.

[1] M. Valtiner, S. Borodin, G. Grundmeier; *Physical Chemistry Chemical Physics,* 9(19), **(2007)** 2406-2412.

[2] M.Valtiner, M. Todorova, G.Grundmeier, and J. Neugebauer; submitted to Physical Review Letters.

[3] M. Valtiner, S. Borodin, G. Grundmeier; *Langmuir,* 24(10),**(2008)** 5350-5358.

5:20pm **SS2-TuA11 Electronic Structure of Zinc and Free-Base Tetraphenylporphyrin Derivatives Adsorbed on TiO_2(110) and ZnO(11-20) Surfaces for Application in Dye Sensitized Solar Cells**, ***S. Katalinic***, *S. Rangan, R. Thorpe, R.A. Bartynski, J. Rochford, K. Chitre, E. Galoppini*, Rutgers University

Metalloporphyrins play an essential role in photosynthetic mechanisms and therefore are natural candidates for electron transfer mediator in dye sensitized solar cells (DSSCs). Among the possible metalloprophyrins, the zinc tetraphenylporphyrins (ZnTPP) derivatives have been found to have similar electron injection and charge recombination properties as the important standard ruthenium dye N3 for DSSCs, as well as reasonable performances using TiO_2 or ZnO as substrates.

Due to a strong decoupling of the meso-phenyls from the main porphyrin macrocycle, the optical absorption properties of the ZnTPP derivatives are found relatively insensitive to the meso-phenyls functionnalization. As a consequence, the adsorption geometry on the surface, as well as the molecule-molecule interaction, can be altered independently of the absorption properties.

Using direct and inverse photoemission spectroscopy we have measured the occupied and unoccupied electronic states of several zinc (and free-base for comparison) tetraphenyporphyrin derivatives adsorbed on single crystals TiO_2 and ZnO surfaces. From this, the alignment of the molecular levels (in particular the frontier orbitals) with respect to the substrate band edges can be directly determined. For a full interpretation of the electronic structure of such molecular adsorbates, we have compared our measurements to ab-initio calculations of the density of states. In addition to spectroscopic surface averaged probes, we have used scanning tunneling microscopy to study the local bonding geometries at the surface of the semiconductors. Recent results will be presented and compared to those available in the literature.

Surface Science
Room: N - Session SS3-TuA

Catalysis: Mechanisms & Morphology
Moderator: B.R. Cuenya, University of Central Florida

2:00pm **SS3-TuA1 High Catalytic Activity of CeO_x/Au(111) and Au/CeO_x/TiO_2(110): Special Properties of CeO_x Nanoparticles**, ***J.A. Rodriguez***, *J.B. Park, J. Graciani,* Brookhaven National Laboratory, *J. Evans,* Universidad Central de Venezuela, *D.J. Stacchiola, S.J. Ma, P.J. Liu,* Brookhaven National Laboratory, *J. Fdez-Sanz,* Universidad de Sevilla, Spain, *J. Hrbek*, Brookhaven National Laboratory **INVITED**

This talk will focus on a series of studies investigating the catalytic activity of CeO_x/Au(111) and Au/CeOx/TiO_2(110) for the water-gas shift (WGS, CO + H_2O --> H_2 + CO_2) reaction and CO oxidation. Au(111) is inactive for the WGS. The deposition of ceria nanoparticles on Au(111) produces a highly active WGS catalysts. An even better catalysts is produced after depositing Au and CeOx nanoparticles on TiO_2(110). The titania substrate imposes non-typical coordination modes on the ceria nanoparticles. In the CeO_x/TiO_2(110) systems, the Ce cations adopt an structural geometry and an oxidation state (+3) which are quite different from those seen in bulk ceria or for ceria nanoparticles deposited on metal substrates. The increase in the stability of the Ce^{3+} oxidation state leads to an enhancement in the chemical and catalytic activity of the ceria nanoparticles. The co-deposition of ceria and gold nanoparticles on a TiO_2(110) substrate generates catalysts with an extremely high activity for the production of hydrogen through the WGS or for the oxidation of carbon monoxide. The exploration of mixed-metal oxides at the nanometer level may open new avenues for optimizing catalysts through stabilization of unconventional surface structures with special chemical activity.

2:40pm **SS3-TuA3 Kinetics and Elementary Steps of the Reverse Water-Gas Shift Reaction over Pt Catalysts**, *L.G. Cameron,* ***C.T. Campbell***, University of Washington, *L. Grabow, M. Mavrikakis*, University of Wisconsin

The kinetics of the reverse water gas shift (RWGS) reaction (CO_2 + H_2 → CO + H_2O) have been measured over clean and annealed Pt powder at a variety of conditions, and the surface coverage of adsorbed intermediates was verified by transient techniques. Under conditions were the surface coverage is very low and the reaction is occurring on essentially adsorbate-free Pt, the RWGS rate is 1000-fold faster than the rate of dissociative CO_2 adsorption ($CO_2 \rightarrow CO + O_{ad}$), estimated from measurements of the reverse rate and equilibrium constant for this elementary step. This proves that the dominant mechanism for the RWGS reaction is not via dissociative CO_2 adsorption. The energetics estimated from DFT calculations of potential alternate pathways on Pt(111) suggests that CO_2 is instead activated by reaction with H_{ad} to make a $COOH_{ad}$ intermediate, which dissociates to make CO_{ad} and OH_{ad}. A microkinetic model based on these DFT energetics reproduces well the measured absolute rate per Pt atom, its activation energy, and its dependences on CO_2 and H_2 partial pressures. This offers strong support for this alternate "carboxylate" pathway as dominating the mechanism. Estimates of the degrees of rate control of this reaction's elementary steps and intermediates will also be discussed.

Work supported by DOE-OBES Chemical Sciences Division.

3:00pm **SS3-TuA4 A DFT Study of Methanol Synthesis by CO_2 Hydrogenation on Cu Nanoparticles and Surfaces**, ***Y. Yang***, SUNY at Stony Brook, *P.J. Liu, M. White*, Brookhaven National Laboratory

The synthesis of methanol from CO_2 and H_2 ($CO_2+3H_2 \rightarrow CH_3OH+H_2O$) has attracted considerable attention. It is not only environmentally important due to its application in the conversion of greenhouse gas, CO_2, it is also of great industrial significance because the product, methanol, can serve as a raw material for the synthesis of other organic compounds, besides being used as a liquid fuel. Commercially, the reaction is performed on a catalyst containing Cu, ZnO and Al_2O_3 at a high temperate (220-240°C) and high pressure (50-100 bar). There is a need to understand the reaction mechanism in order to develop more active and selective catalysts even though the mechanism is still controversial. In this study, density functional theory (DFT) was employed to elucidate the reaction mechanism on the Cu(111) surface and the promotion effect of nano-size Cu compared to bulk Cu.

Cu_{29} nanoparticles, exposing a combination of (100) and (111) faces in a pyramidal structure, is the model we used to study the reaction pathways on the Cu nanoparticles. For comparison, the reaction mechanism on the Cu(111) surface is also studied. It was found out that on both systems, the reaction undergoes via formate (HCOO) and dioxomethylene (H_2COO). The reaction rate is controlled by hydrogenation of HCOO and H_2COO. In accordance with experimental findings, our results show that the Cu_{29} nanoparticles display a superior activity over Cu(111). The better behavior of Cu_{29} is associated with the low-coordinated Cu sites, which provide a reasonably strong binding to the intermediates.

v

4:00pm **SS3-TuA7 Electronic Structure Effect in Modified Reactivity of Pt/Cu(111)**, ***T. Anniyev***, *S. Kaya, H. Ogasawara,* Stanford Synchrotron Radiation Lightsource*, S. Koh, P. Strasser,* University of Houston*, M. Toney, A. Nilsson*, Stanford Synchrotron Radiation Lightsource

A key role in the activity of transition metal catalysts is the degree of interaction of metal d-bands with the adsorbed atoms/molecules [1]. It has been suggested that d-band center is a single effective measure of this interaction [2]. In this work we demonstrate how strain induced electronic structure changes can be used to tune the catalytic activity of the Oxygen Reduction Reaction (ORR). The limiting factor in the performance of the Pt-based PEM fuel cells is the low rate of the ORR taking place at the cathode. It has recently been shown that electrochemically leached PtCu catalysts, which have strained Pt rich shell due to dissolution of Cu, exhibit uniquely high reactivity for this reaction [3] . Using a surface science approach we have investigated the electronic structure effect in the enhanced ORR activity using Pt monolayers epitaxially grown on Cu(111) as a model system. We show that compressive strain and host substrate-induced changes in the Pt d-band center are responsible for the changes in chemisorption strength of adsorbed oxygen. Electronic nature of chemisorbed oxygen atoms on strained Pt monolayers has been investigated by probing oxygen projected density of states below and above the Fermi level using X-ray emission spectroscopy (XES) and X-ray absorption spectroscopy (XAS), respectively. Combined oxygen K-edge XAS and XES results of oxygen on strained Pt monolayers show lowering of the adsorbate projected density of states and a complete filling up of antibonding states above Fermi level indicative of weakened metal-oxygen bond relative to that of oxygen on Pt(111). The weakening of the metal-oxygen bond is correlated with the broadening and lowering of the Pt d-band probed by valence band X-ray photoemission spectroscopy (XPS). The observed results are explained in terms of the d-band model.

References

[1] B. Hammer and J. K. Norskov, Theoretical surface science and catalysis—calculations and concepts, Adv. Catal. 45, 71 (2000).

[2] G.A. Somorjai, Introduction to Surface Chemistry and Catalysis (John Wiley & Sons, New York, 1994).

[3] S. Koh and P. Strasser, Electrocatalysis on bimetallic surfaces: Modifying catalytic reactivity for oxygen reduction by voltammetric surface de-alloying, J. Am. Chem. Soc., 129 (42), 12624-12625 (2007).

4:20pm **SS3-TuA8 In Situ Study of Heterogeneous Catalysis on Oxide Support: CO Oxidation on Au/TiO_2 Catalysts**, ***S. Porsgaard,*** Lawrence Berkeley National Lab and University of Aarhus, Denmark*, P. Jiang, F. Borondics, M. Köber,* Lawrence Berkeley National Lab*, S. Wendt,* University of Aarhus, Denmark*, H. Bluhm,* Lawrence Berkeley National Lab*, F. Besenbacher,* University of Aarhus, Denmark*, M. Salmeron*, Lawrence Berkeley National Lab

It has been known for more than a decade that the system of gold nanoparticles on a TiO2 support (Au/TiO2) is an active catalyst for a variety of reactions even below room temperature.[1] However, there is still little agreement on several important questions such as the role of the substrate, the charge state of gold, and the role of oxygen vacancies, even for the simplest reaction of CO oxidation.

In this study we focus on the questions related to the electronic band structure of the substrate. We chose a model system of evaporated Au nanoparticles on a rutile TiO2(110) single crystal substrate. The morphology of the evaporated Au nanoparticles were studied by STM, and it turned out to be strongly dependent on the pre-treatment of the TiO2 surface.[2]

For traditional surface science, the pressure gap between the studies in ultra high vacuum (UHV) and the industrial relevant reaction conditions is an important challenge. To overcome this problem, we have used in situ X-ray Photoelectron Spectroscopy (in situ XPS)[3] to study the evolution of the adsorbed chemical species and the electronic band structure of the rutile TiO2(110) during the individual steps in the reaction under pressures up to 1 Torr.

However, XPS on semiconductor substrates is challenging especially in the presence of gases. We have designed novel samples and test experiments to overcome these drawbacks. These results show that most in situ experiments on semiconductor substrates require extraordinary precautions. Now, we are able to avoid the newly discovered pitfalls, and we are able to present decisive results on the previously debated problems, e.g. the ongoing discussion about the charge state of gold and the role of oxygen vacancies.

[1] M. Haruta, S. Tsubota, T. Kobayashi, H. Kageyama, J.M. Genet , and B. Delmon, "Low-Temperature Oxidation of CO over Gold Supported on TiO2, α-Fe2O3, and Co3O4," Journal of Catalysis, vol. 144, Nov. 1993, pp. 175-192.

[2] D. Matthey, J. Wang, S. Wendt, J. Matthiesen, R. Schaub, E. Laegsgaard, B. Hammer, and F. Besenbacher, "Enhanced bonding of gold nanoparticles on oxidized TiO2(110)," SCIENCE, vol. 315, Mar. 2007, pp. 1692-1696.

[3] D. Ogletree, H. Bluhm, G. Lebedev, C. Fadley, Z. Hussain, and M. Salmeron, "A differentially pumped electrostatic lens system for photoemission studies in the millibar range," REVIEW OF SCIENTIFIC INSTRUMENTS, vol. 73, Nov. 2002, pp. 3872-3877.

4:40pm **SS3-TuA9 Search for Chemicurrent during CO Oxidation on Pt/GaN and Pt/TiO_2 Nanodiodes**, ***J.R. Creighton***, *E.J. Heller, K.H.A Bogart, M.E. Coltrin, E.N. Coker, K.C. Cross*, Sandia National Laboratories

In 2005, Gabor Somorjai's group demonstrated the capture of chemical energy liberated during carbon monoxide oxidation on Pt and Pd surfaces by using a structure they described as a "catalytic nanodiode" [1-2]. This device is a Schottky diode where the metal contact is made of an ultrathin (~5 nm) catalytic metal, deposited on a wide bandgap semiconductor such as GaN or TiO_2. During the exothermic oxidation of CO, some fraction of the chemical energy may be dissipated by creation of hot electrons in the catalytic metal, and some of these electrons are potentially collected on the semiconductor side of the Schottky barrier. In principle, this "chemicurrent" formed by hot electron generation, transport, and collection represents the conversion of chemical energy directly into electrical energy. For some conditions using a Pt/TiO_2 nanodiode, a remarkable conversion efficiency of 3 electrons per 4 CO_2 produced was measured [1]. We have fabricated several versions of catalytic nanodiodes using GaN and TiO_2 films deposited and characterized in-house. During CO oxidation on Pt/GaN and Pt/TiO_2 nanodiodes we also detect a current that is unambiguously a result of the chemical reaction. We measure current densities up to 100 nA/mm^2 and reaction conversion efficiencies in the range of 10^{-5}-10^{-3} electrons per CO_2, which are quantitatively similar to reports in more recent publications [3-4]. However, the behavior of this chemical signal as a function of diode impedance indicates that it is derived from a **voltage source**, and not from a current source. In fact, the chemical signal is primarily, if not entirely, due to the thermoelectric voltage generated and/or modified by the exothermicity of the reaction. We have yet to find any conclusive evidence supporting true “chemicurrent” formation during CO oxidation on Pt/GaN or Pt/TiO_2 nanodiodes.

References:

[1] Z.J. Xiao and G.A. Somorjai, J. Phys. Chem. B 109 (2005) 22530.

[2] J. Xiaozhong, A. Zuppero, J.M. Gidwani, and G.A. Somorjai, J. Amer. Chem. Soc. 127 (2005) 5792.

[3] J.Y. Park, J. R. Renzas, B.B. Hsu, and G.A. Somorjai, J. Phys. Chem. C, 111 (2007) 15331

[4] J.Y. Park, J. R. Renzas, A.M. Contreras, and G.A. Somorjai, Topics in Catalysis, 46 (2007) 217

(Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy under Contract DE-AC04-94AL85000.)

5:00pm **SS3-TuA10 MORTON S. TRAUM AWARD FINALIST: Morphology and Chemical Reactivity of Bi-Metallic Au-Pd Clusters**, ***E. Gross****, *M. Asscher*, The Hebrew University of Jerusalem, Israel

Bi-metallic clusters have unique catalytic properties, since one metal can modify the electronic and thus the catalytic properties of the other metal. Here we describe a unique preparation method of bimetallic Pd-Au nano-clusters. The growth mode is based on initial evaporation of metal atoms on top of amorphous solid water adsorbed on SiO_2/Si(100) substrate at 100K under ultra high vacuum (UHV) conditions. The ice buffer layer separates the small metallic seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth of nano-clusters in a Buffer Layer Assisted Growth (BLAG) mechanism.

Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) measurements revealed that by modifying the clusters preparation procedure either segregated or alloyed Pd-Au clusters can be formed. The composition of the different clusters was also verified by optical surface plasmon resonance (SPR) absorption measurements.

Temperature Programmed Reaction (TPR) measurements have shown that adsorption of acetylene on top of Pd-Au alloy clusters has led to efficient conversion to ethylene. Benzene was also formed at an order of magnitude smaller rate. Pd-Au alloy clusters have demonstrated significantly higher reactivity than the monometallic clusters. Increasing the surface defects density by Ar^+ ion sputtering enhanced the thermal stability and sintering resistance properties of the Pd-Au clusters.

5:20pm **SS3-TuA11 Reactivity of NO_2 with BaO Nanoclusters Grown on YSZ(111) and CeO_2(111)/YSZ(111) Probed by *in situ* High-Resolution XPS**, ***Z.Q. Yu***, Nanjing Normal University, China, *P. Nachimuthu,* Pacific Northwest National Laboratory, *M. Nandasiri, S.V.N.T. Kuchibhatla,* Pacific Northwest Natioanl Laboratory, *Y.J. Kim,* Hanbat National University, Korea, *M.H. Engelhard, V. Shutthanandan, W. Jiang, J. Szanyi, S. Thevuthasan*, Pacific Northwest National Laboratory

Catalysts for NO_x storage and reduction (NSR) are being developed to reduce the NO_x emission from gasoline based internal combustion engines. BaO is considered to be potential NSR catalysts because of its strong interaction and an effective trapping of NO_2. BaO is more reactive when BaO is present as non-stoichiometric BaO clusters rather than bulk BaO. In order to understand the reactivity, BaO was grown on YSZ(111) and CeO_2(111)/YSZ(111) substrates by molecular beam epitaxy. *In-situ* reflection high-energy electron diffraction, *ex-situ* x-ray diffraction, atomic force microscopy and x-ray photoelectron spectroscopy have confirmed that the BaO grows as nanoclusters on YSZ(111) . During and following the growth under UHV conditions, BaO remains in single phase. The reaction of NO_2 with the BaO nanoclusters in different sizes on YSZ(111) and CeO_2(111)/YSZ(111) substrates was investigated using *in situ* high-resolution x-ray photoelectron spectroscopy (XPS). The adsorption of NO_2 on the BaO nanoclusters at room temperature and the formation of $Ba(NO_x)_2$ species at room temperature and above were probed. In addition the *in situ* XPS data collected from the BaO nanocluesters prior to and following the reaction with NO_2 were utilized to understand the morphology of BaO nanoclusters and the formation of $Ba(NO_x)_2$ species using Quases-Tougaard V5.1 software. These results are compared with the reported data from NO_2 reaction with BaO film deposited onto an Al_2O_3/NiAl(110) substrate.

Thin Film
Room: B3 - Session TF1-TuA

Computational Modeling and Analysis of Thin Films
Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

2:00pm **TF1-TuA1 First Principles Modeling of Hydrogen Diffusion in Thin Films: Crystalline Alloys, Amorphous Alloys, and Metal Hydrides**, ***D. Sholl***, *S. Hao, L. Semidey-Flecha, C. Ling, S.-G. Kang*, Georgia Institute of Technology **INVITED**

The diffusion of hydrogen through thin films is important in a variety of technological applications, including development of membranes for hydrogen purification and control of hydrogen uptake in solid state storage materials. First principles calculations can play an important complementary role to experimental studies of these phenomena. Examples will be discussed of using first principles approaches in combination with cluster expansions and kinetic Monte Carlo to predict hydrogen permeation rates through crystalline and amorphous metal alloys used as membranes. In these materials, hydrogen exists as an uncharged interstitial atom. We will also discuss the diffusion mechanisms of hydrogen in ionic metal hydrides such as magnesium hydride and simple borohydrides. Understanding the diffusion mechanisms that exist in these materials has created opportunities for enhancing hydrogen transport rates in this important class of materials.

3:00pm **TF1-TuA4 A Family of High Strength Ternary Titanium and Vanadium Nitride Thin Films**, *D.G. Sangiovanni,* ***V. Chirita***, *L. Hultman*, Linkoping University, Sweden

We use Density Functional Theory (DFT) calculations in the generalized gradient approximation (GGA) to predict the properties of a number of novel Ti-M-N and V-M-N thin films in the B1 (NaCl) structure. The new compounds are obtained by alloying TiN and VN, with Ta, Nb, V, Mo and W, respectively Nb and W, in concentrations of 50 %. We evaluate the elastic moduli and constants for all these ternaries, perform a detailed analysis of their electronic structure, and compare these results with the corresponding properties of TiN and $Ti_{0.5}Al_{0.5}N$. Our calculations show that, in terms of hardness, these ternaries compare with TiN and $Ti_{0.5}Al_{0.5}N$, as we obtain comparable, respectively increased values, for the Young and bulk moduli, in most cases. Significantly, however, these novel compounds exhibit substantially lower values of the C_{44} elastic constant and positive Cauchy pressures, i.e. they are considerably more ductile than TiN and $Ti_{0.5}Al_{0.5}N$. This unique combination of increased hardness and ductility, which is in contrast to the hardness/brittleness relationship typically found in hard coatings, is certainly relevant for applications in which high strength thin films/coatings are desired. In terms of electronic structure, our results reveal a layered charge density for all these ternaries, consisting in alternating high and low electron density regions, similar to that reported for MAX phase materials and other nanolaminates. This combination of metallic and ceramic properties is also evident in the density of states analysis we report. In order to fully understand the mechanism responsible for this interleaved arrangement of electrons, we carry out an improved crystal orbital overlap population (COOP) calculation and succeed in resolving energetically the bonding and antibonding contributions, of the first and second neighbors, to the chemical bonds in these compounds. Herein, we present the results of our COOP analysis, and based on this, we explain the observed trend in hardness and ductility as a result of the interaction between the e_g and t_{2g} sets of d orbitals characteristic to these ternaries.

4:00pm **TF1-TuA7 Study on the Influence of Ballistic and Diffusive Deposition Particles on the Evolution of the Surface Morphology of Thin Films**, ***R. Alvarez***, *P. Romero-Gomez, J. Gil-Rostra, A. Palmero, J. Cotrino, F. Yubero, A.R. Gonzalez-Elipe*, CSIC - University of Sevilla, Spain

The influence of ballistic and diffusive particles on the development of the surface morphology of plasma-assisted sputtered thin films is studied. Ballistic particles are sputtered from the cathode and are characterized by their high directionality towards the film surface as well as by typical kinetic energies in the order of 1 eV, whereas thermal diffusive particles follow the Maxwell velocity distribution function, with typical kinetic energies in the order of 0.01 eV. These factors influence the role of non-local surface shadowing and the surface sticking probability of the deposition particles, which, along with other fundamental mechanisms, strongly condition the development of the film morphology. In order to carry out this research, a combined theoretical and experimental approach has been followed: on one hand several thin films have been deposited in different experimental conditions which allow differentiating ballistic and diffusive contributions to the film growth, and, on the other hand, we have

---

* Morton S. Traum Award Finalist

developed a basic Monte Carlo model of the depositions process. The comparison between experimental and theoretical results provides fundamental understanding about the influence of ballistic and diffusive particles on the development of the thin film nanostructure.

4:20pm **TF1-TuA8 DSMC Modeling of E-beam Metal Deposition**, *V. Ayyaswamy*, ***A. Alexeenko***, Purdue University

Electron-beam assisted physical vapor deposition (EBPVD) is now used in a wide variety of vacuum material processing applications for generation of thin films of metals and metallic compounds. The thickness uniformity, growth rates, grain size, stoichiometry and other material properties of EBPVD thin films are highly dependent on the specifics of the system such as, for example, the geometric configuration and energy density of electron gun. A general capability to model the metal vapor flows encountered in EBPVD processes can greatly assist in the design and control of such deposition systems and processes. The main goal of this paper is to apply the direct simulation Monte Carlo (DSMC) method for modeling of a typical strip EBPVD system.

Under the conditions of high energy electron-beam deposition in ultra-high vacuum, the flow of metal vapor in EBPVD systems varies from high-density collisional flow in the proximity of the source to free-molecular flow at the deposition site. The application of the DSMC method for such flows requires a model for metal atom and cluster collisions. In this work, a model for copper-copper collisions is formulated and validated by comparison with experimentally measured deposition data reported by Sahu and Thakur (2006). The proposed molecular model can be used in DSMC simulations for the prediction of growth rates in thin film depositions of copper thereby leading to a more efficient designs of such deposition systems.

4:40pm **TF1-TuA9 Electrochemical Capacitance in Cerium Oxide Thin Films and Its Relations to Anionic & Electronic Defects**, ***W. Chueh***, *S. Haile*, California Institute of Technology

The electronic properties of thin film oxides are relevant in a broad range of phenomena and devices. In many instances, these properties are strongly influenced by the extent of deviation of the material stoichiometry away from that of the perfect crystal. Specifically, nonstoichiometry in oxides due to the formation of point defects can substantially impact electrical, electrochemical, and optical properties of thin films. However, the small sample mass and the constraints of a substrate hinder precise measurements, particularly with respect to the determination of oxygen nonstoichiometry, and, effectively, electronic carrier concentration. Even a relatively straightforward Hall effect measurement is precluded in the case of low mobility materials (typical of solid electrolytes). Thus, a reliable and highly accurate method for determining nonstoichiometry and carrier concentration in thin film oxides may be useful for a number of fields.

In this work, we show that it is possible to accurately determine oxygen nonstoichiometry and electronic carrier concentration in epitaxial nonstoichiometric samarium doped ceria thin films from an analysis of the capacitance measured by electrochemical impedance in a cross-plane configuration. For sufficiently thick bulk samples, it has been shown that a "chemical capacitance" arises from the change in the oxygen nonstochiometry in response to the change in the oxygen chemical potential, analogous to the change in the polarization of a dielectric in response to the change in electric potential in an electrostatic capacitor. We extend this method to thin films and show that both interfacial and chemical capacitances contribute strongly to the observed capacitance and successfully decouple the two. The thin film oxygen nonstoichiometry and electronic defect concentration determined using chemical capacitance corresponds closely to bulk values in literature.

5:00pm **TF1-TuA10 Virtual Sputter Chamber - Multiphysics Simulation of Magnetron Sputter & Deposition**, ***C. Walton***, *G. Gilmer, M. McNenly,* Lawrence Livermore National Laboratory*, J. Verboncoeur,* University of California*, S. Wilks, L. Zepeda-Ruiz, T.W. Barbee*, Lawrence Livermore National Laboratory

Lack of detailed process conditions knowledge remains a key challenge in magnetron sputtering, both for chamber design and for process development. Fundamental information such as the pressure and temperature distribution of the sputter gas, and the energies and arrival angles of the sputtered atoms and other energetic species is often missing, or is only estimated from general formulas. However, open-source or low-cost tools are available for modeling all the physics of the sputter process, which can give more accurate data from desktop computations than traditional empirical approaches.

To get a better understanding of magnetron sputtering, we have collected existing models for the 4 main physics steps: 1) dynamics of the plasma using Particle In Cell-Monte Carlo Collision (PIC-MCC), 2) impact of ions on the target using molecular dynamics (MD), 3) transport of sputtered atoms to the substrate using Direct Simulation Monte Carlo (DSMC), and 4) growth of the film using hybrid Kinetic Monte Carlo (KMC) and MD methods. All the models have been tested against experimental measurements. The spatial distribution and electron temperature T_e of the plasma have been reproduced within ~25% for a scaled model of an example magnetron system. The rarefaction of the neutral gas in front of a magnetron observed by Rossnagel and others has been reproduced, and it is associated with a local pressure increase of ~50% which may strongly influence film properties such as stress and film density. Results on energies and arrival angles of sputtered atoms and reflected gas neutrals are applied to the Kinetic Monte Carlo simulation of film growth. Model results and applications to growth of Cu, Zr and Be films will be presented. Work underway on increasing computation speed with parallelization will also be discussed.

5:20pm **TF1-TuA11 Tuning Knobs for the Morphology and Dewetting of a Bimodal Molecular System**, ***J. Topple***, McGill University, Canada*, S. Burke,* UC Berkeley*, S. Fostner, P. Grutter*, McGill University, Canada

The interesting optical and electronic properties of certain organic molecules have led to their use in a range of organic electronic and optoelectronic applications. The morphology of thin films critically determines application relevant properties, and can be controlled during growth to some degree by experimental parameters. However, post-growth dynamics may change the film structure and resulting properties. We explore methods of tuning film morphology and the rate of dewetting through coverage, surface templating and temperature control. Non-contact atomic force microscopy (NC-AFM) is a non-destructive, high resolution scanning probe technique that can be applied to non-conductive surfaces. Perylene derivatives have been studied as prototypal organic semiconductors for use in electronic applications. Deposition of sub-monolayer coverages of 3,4,9,10-perylenetetracarboxylic diimide onto NaCl (001) at room temperature results in the bimodal growth of coexisting square and needle shaped islands. The epitaxy of each island type was determined from molecular and atomic resolution NC-AFM images. Post-deposition, the stable needle islands grow while the metastable square islands disappear completely within days. This is characterized as a dewetting transition, the dynamics of which have been described and empirically fit to the monomolecular growth model. The resultant island distribution, size, and rate of dewetting may be tuned by templating the NaCl substrate with single atomic layer deep pits, depositing gold nanoclusters, or a combination of the two to modify island nucleation. The diffusion lengths may be altered by varying the substrate temperature. This characterization is an important step in controlling the structure of thin organic films for nanoscale devices which are sensitive to the nanoscale film structure.

Thin Film
Room: B4 - Session TF2-TuA

ALD/CVD: Oxides and Barriers
Moderator: S.M. Rossnagel, IBM Research

2:20pm **TF2-TuA2 Evaluation of Al_2O_3 ALD Gas Diffusion Barriers and Visualization of Barrier Defects Using the Ca Test**, ***J.A. Bertrand***, *S.H. Jen, D. Seghete, S.M. George*, University of Colorado, Boulder

Flexible gas diffusion barriers are required on polymers. One key application area for these barrier films is organic electronics, especially organic light emitting diodes (OLED) for flexible displays.The necessary water vapor transmission rate (WVTR) for OLEDs is $<10^{-6}$ g/m^2/day. In collaboration with DuPont, we earlier measured low WVTR values of ~6.5 x 10^{-5} g/m^2/day for single Al_2O_3 ALD films at 60°C/85% RH using the Ca test with optical transmission probing (*Appl. Phys. Lett.*89, 031915 (2006)). Our current measurements have employed the Ca test with electrical resistance probing. The electrical resistance probing method is based on previous work by Paetzold and coworkers (*Rev. Sci. Instrum*. 74, 5147 (2003)). The change of the electrical resistance of the Ca film versus time can be related to the WVTR.

The current results are also obtained using a new ALD reactor that is connected to a glove box that is interfaced to a PVD chamber. This apparatus allows Ca test films to be prepared, transferred into the glove box and then positioned in the ALD reactor all under oxygen-free conditions. The glove box also helps to reduce particle contamination that may be the dominant factor in determining the WVTR. Using this apparatus, we have measured even lower WVTR values of ~2 x10^{-5} g/m^2/day at 70oC/28% RH with an Al_2O_3 ALD film thickness of 25 nm. This is the lowest WVTR value measured at elevated temperature for a single layer barrier film.

The Al_2O_3 ALD barriers are also deposited directly on the Ca films. This configuration allows the Ca test film to visualize the defects in the Al_2O_3 ALD barrier. As the calcium oxidizes, the transition from shiny metal to clear calcium oxide can monitor the number and distribution of defects in the Al_2O_3 ALD film. The experiments demonstrate that the calcium oxidation is dominated by a few pinhole defects. The WVTR value of ~2 x 10^{-5} g/m^2/day is consistent with several defects per cm^2 in the Al_2O_3 ALD film. The resistance increases as these pinholes lead to the oxidation of circular regions of the Ca film that grow with time.

2:40pm **TF2-TuA3 Atomic Layer Deposition of TiO_2 on Si (100) and GaAs (100) Surfaces**, ***T. Gougousi***, *J.W. Lacis*, UMBC, *J.D. Demaree*, ARL

Atomic Layer Deposition (ALD) has been used to deposit TiO2 films on Si (100) and GaAs (100) surfaces from tetrakis dimethylamino titanium (TDMATi) and H2O at 200°C. The growth rate is measured at ~.6Å/cycle by High Resolution Transmission Electron Microscopy (HRTEM) and spectroscopic ellipsometry, and Rutherford Backscattering measurements indicate steady state Ti atom coverage of ~1.4x1015 cm-2. As deposited films are slightly overoxidized (O/Ti~2.2) and are amorphous, but inert anneals above 500°C result in film crystallization mainly in the rutile phase. When films are deposited on native oxide GaAs surfaces an interface cleaning reaction is observed. The starting surface consists of ~26Å of gallium and arsenic native oxides. X-ray photoelectron spectroscopy indicates that the surface oxides are consumed gradually during the ALD process and that after 120 and 250 process cycles only about a monolayer of metallic arsenic-arsenic suboxide and gallium suboxide persists at the interface and the conclusions are corroborated by HRTEM data. The results for the TiO2/GaAs interface will be compared to that obtained for the HfO2/GaAs interface using two different but similar ALD chemistries that utilize amide precursors (TEMAHf and TDMAHf). All three ALD chemistries indicate the presence of an "interface cleaning" mechanism similar to what has been observed for other amide-precursor-based ALD processes. [1] [2] [3]

[1] 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)

[2] C. L. Hinkle, A. M. Sonnet, E. M. Vogel, S. McDonnell, G. J. Hughes, M. Milojevic, B. Lee, F. S. Aguirre-Tostado, K. J. Choi, H. C. Kim, J. Kim, and R. M. Wallace, Appl. Phys. Lett. **92**, 071901 (2008)

[3] J.C. Hackley, J.D. Demaree, and T. Gougousi, Appl. Phys. Lett. **92**(16), 162902 (2008).

3:00pm **TF2-TuA4 Self-limiting Deposition of Anatase TiO_2 for Photocatalytic Applications**, ***N.G. Kubala***, *C.A. Wolden*, Colorado School of Mines

Titanium dioxide thin films were deposited using pulsed plasma-enhanced chemical vapor deposition at low temperature (T_s <200 ºC). Self-limiting deposition (~1 Å/cycle) was accomplished via simultaneous delivery of $TiCl_4$ and O_2. $TiCl_4$ is shown to be inert with molecular oxygen at process conditions, making it a suitable precursor for pulsed PECVD. The process was examined as a function of $TiCl_4$ exposure, plasma power, and substrate temperature. Crystalline anatase formation was observed at temperatures as low as 120ºC. Depositions at high power also had a significantly greater refractive index. For process conditions, digital control over film thickness is demonstrated. Film uniformity is exceptional, with thickness variations less than 1% across 100 mm silicon wafers. Photocatalytic activity has been examined using methylene blue decomposition experiments, UV-VIS spectroscopy, and electrochemical analysis. Mott-Schottky plots show that the band edge position of these thin films is in agreement with measurements from anatase single crystals. The photocatalytic activity of these films for both hydrogen production and organic remediation is assessed. We also plan to present new results on the production of the titania-vanadia alloys with enhanced light response in the visible regime.

4:00pm **TF2-TuA7 *In situ* X-ray Photoelectron Spectroscopy for the Study of Initial Stages of TiO_2 ALD on Silicon**, ***R. Methaapanon***, Stanford University

Titanium dioxide (TiO_2) is one of the widely studied atomic layer deposition (ALD) systems due to its outstanding electrical and optical properties that are suitable for variety of applications. The properties of the deposited TiO_2, especially at the interface with the substrate, become more important as the size of required devices in each application approaches the nano-scale. Due to different chemical properties of the substrate and the deposited material, nucleation at the interface can be different from the steady state growth of the bulk.

In this work, TiO_2 ALD is carried out in an integrated ALD reactor/UHV chamber that allows for X-ray photoelectron spectroscopy (XPS) analysis after each precursor pulse without vacuum break. Titanium tetrachloride ($TiCl_4$) and water (H_2O) are selected as precursors due to their molecular simplicity and broad operating temperature range that result in several achievable TiO_2 phases. The initial growth at 100ºC on two substrates − chemical oxide on silicon prepared by piranha treatment, and hydrogen-terminated silicon prepared by HF etch − is compared. The intensities and binding energies of characteristic peaks from the XPS spectra are used to analyze the elemental compositions and chemical state of each species as the deposition progresses. TiO_2 growth on both SiO_2 and H-Si surfaces exhibits linear behavior, as normally achieved by ALD, but the TiO_2 growth rate is lower on hydrogen-terminated surface than on silicon dioxide surface. Interestingly, no incubation period is observed on either surface.

The chemical shifts of the Si 2p, O 1s and Ti 2p XPS peaks after TiO_2 deposition on the SiO_2 substrate suggest bond formation between titanium and silicon-bound oxygen at the interface. The data also suggest that some chlorine is trapped at the SiO_2/TiO_2 interface and that the titanium oxide right at the interface is sub-stoichiometric. The results on the hydrogen-terminated Si surface show different interfacial properties. There is no detectable amount of oxidized silicon species on hydrogen-terminated silicon after deposition under vacuum. Together with the results of *ex situ* studies, it can be concluded that interfacial silicon dioxide grows after air exposure, not during ALD reactions. The absence of silicon oxide and a shift in the Si 2p binding energy in the as-grown samples suggest the possibility of an ALD mechanism which involves direct bonding between titanium and silicon on the surface. The differences between the two substrates will be discussed.

4:20pm **TF2-TuA8 Plasma-Assisted Atomic Layer Deposition of Titanium Dioxide: Reaction Mechanism Studies using Attenuated Total Reflection Fourier Transform Infrared Spectroscopy**, *V. Rai*, ***S. Agarwal***, Colorado School of Mines

In this presentation, the authors will discuss the surface reaction mechanism during the plasma-assisted atomic layer deposition (ALD) of TiO_2 using titanium tetraisopropoxide and an O_2-Ar plasma at substrate temperatures ≤150 °C. In situ attenuated total reflection Fourier-transform infrared (IR) spectroscopy was used to detect surface species generated or consumed during each half-reaction cycle with a sensitivity down to a fraction of a monolayer. Our IR data showed that the reactive species on the TiO_2 surface for TTIP chemisorption were *both* surface carbonates and –OH groups, identified in the 1450-1700 and 3400-3800 cm^{-1} regions, respectively. Based on this observation, we conclude that plasma-assisted ALD of TiO_2 involves a combination of the mechanisms previously reported for O_3- and H_2O-based ALD using TTIP as the metal precursor: we had recently reported surface carbonates as the reactive sites using O_3 as the oxidizing agent and –OH groups have previously been reported with H_2O as the oxidant. We hypothesize the following reaction mechanism. Combustion products such as CO_2, CO, and H_2O are formed during the O_2-plasma cycle due to the plasma-assisted combustion of the isopropoxy ligands on the surface. A fraction of this CO_2 reacts with the surface to generate the carbonates, similar to the O_3-based ALD mechanism. We explain the simultaneous presence of the surface –OH groups in addition to the carbonates due to the plasma activation of H_2O, also generated during the O_2 plasma cycle, and the subsequent reaction of these activated species with the surface. The latter step does not occur when O_3 is used as the oxidant. In fact, the ratio of the carbonates and the surface –OH groups could be varied by controlling the residence time of the reaction products in the plasma. A growth per cycle of ~0.8 Å was obtained at 150 °C, which was significantly higher compared to H_2O- and O_3-based ALD of TiO_2 at similar temperatures. In situ and ex situ IR measurements showed no significant carbon contamination in the films. Ex situ IR data showed the Ti-O-Ti transverse optic mode at 440 cm^{-1}, a characteristic of anatase. The ex situ x-ray diffraction measurements further confirmed anatase as the dominant crystal phase. The crystallinity of the films may be the reason for the higher growth per cycle compared to that observed for amorphous films deposited from the same metal precursor.

4:40pm **TF2-TuA9 Molecular Layer Deposition of "Sugarcone" Hybrid Organic-Inorganic Films Using Saccharides and Metal Precursors**, ***B. Yoon***, *R. Hall, D. Seghete, A.S. Cavanagh, S.M. George*, University of Colorado at Boulder

Molecular layer deposition (MLD) of hybrid organic-inorganic polymers is based on the sequential, self-limiting reactions of organic and inorganic reactants. Alucone MLD has been reported based on the reaction between trimethylaluminum (TMA) and ethylene glycol (EG). Zincone MLD has also been demonstrated using diethylzinc and EG as the reactants. In this study, a new class of hybrid organic-inorganic films that can be called "sugarcone" was fabricated based on the reaction between saccharides and metal reactants. This strategy was demonstrated using sucrose and TMA.

The sugarcone MLD film growth was monitored using in situ transmission FTIR analysis. The FTIR spectra revealed that TMA reacts with hydroxyl groups and deposits $AlCH_3$* species. The sucrose then reacts with the $AlCH_3$* species and deposits an organic moiety with available hydroxyl groups. Both the TMA and sucrose sequential reactions were self-limiting. Sequential exposures of TMA and sucrose led to the linear growth of the sugarcone film. X-ray reflectivity measurements were consistent with a growth rate of ~ 2.0 Å per cycle based on 300 MLD cycles on a Si wafer at 150°C. The TEM images of sugarcone films on ZrO_2 nanoparticles after 150 MLD cycles at 150°C were in agreement with a MLD growth rate of ~2.3 Å per cycle. The sugarcone films were not stable in air and oxidized by adsorbing H_2O. This reaction may be useful in gas diffusion barriers because the sugarcone film could serve as a chemical getter to adsorb any H_2O that diffuses through the barrier.

5:00pm **TF2-TuA10 *In-situ* Half-Cycle XPS Investigation of La-aluminate Formation during Atomic Layer Deposition**, ***T.J. Park***, *H.C. Kim, M. Milojevic, B. Lee, R.M. Wallace, J. Kim,* University of Texas at Dallas*, X. Liu, M. Rousseau, J.H. Li, H. Li, D. Shenai, J. Suydam*, Dow Electronic Materials

Lanthanum based oxide (La_2O_3) having outstanding high dielectric constant of 30 has been extensively investigated because it can provide a generous thickness margin as well as a considerable leakage current reduction which is essentially required in modern device applications. However, the hygroscopic and catalytic nature of La ions lead s to formation of either La-hydroxide ($La(OH)_3$) or La-silicate ($LaSiO_x$) resulting in degradation of device properties. The formation of La-hydroxide can cause serious issues such as shifting of flat band voltage (V_{fb}), increased gate leakage and increased the surface roughness. La-hydroxide may also cause a CVD reaction, ruining the self-limited nature of ALD reaction during conventional water based ALD process. Also, direct deposition of La_2O_3 on Si substrate has a significant amount of La-silicate phase in the grown film by the interfacial reactions with the Si. In order to overcome these intrinsic problems of pure La-oxide, some of researches have been carried out using an addition of aluminum oxide (Al_2O_3) layer in the pure La_2O_3 film. La-aluminate is potentially stable on Si substrate having less opportunity to form an interfacial layer. In addition, La-aluminate has enhanced stability to water ambient due to a gettering effect of Al_2O_3. In this presentation, we will focus on the detailed growth mechanisms of La-aluminate during a water based ALD process. In order to investigate initial interfacial reactions during ALD, we investigate *in-situ* half cycle reactions by means of x-ray photoelectron spectroscopy analysis following individual ALD pulses of tris(N,N'-diisopropylformamidinato) lanthanum $[La(^iPrfAMD)_3]$, trimethyl-Al (TMA) and water (H_2O) at a deposition temperature of 300°C. The La-aluminate sample was transferred from an ALD reactor after every individual pulse of La, Al and H_2O to a monochromatic x-ray photoelectron spectroscopy (XPS) chamber via ultra high vacuum (UHV) chamber maintaining a vacuum level of less than 10^{-11} torr. This experimental technique enables us to investigate evolution of chemical binding status without exposure to air as the number of ALD half cycle increases. Additionally, residual C and N in the films will be also discussed.

5:20pm **TF2-TuA11 Engineering Optical Properties by Controlling Concentration and Proximity of Rare Earth Dopants in an Y_2O_3 Host using Radical Enhanced ALD**, ***J. Hoang***, *J. Chang*, University of California, Los Angeles

The realization of compact fiber optic networks is limited by the control of the rare earth (RE) dopant ion's identity and its distribution. Each RE ion contains spectral energy levels, whose transitions can be promoted by controlling the ion-ion proximity. In this work, a radical enhanced atomic layer deposition (RE-ALD) process, utilizing highly reactive radicals to activate surface reactions, is developed to design complex metal oxides with multiple dopants, whose concentration variation and spatial distribution control enable the synthesis of a wide range of multifunctional materials with tunable properties including magnetic, spectral, and electronic. Specifically, the control of dopant proximity and concentration is used to enhance desirable spectral transitions related to amplification at 1.54 micron for compact planar optical amplifier applications. The spatial distributions between Er^{3+} and various rare earth sensitizers (e.g. Yb and Eu) are investigated. The ability to control the spacing of each sensitizer allows for a unique study of the correlation between energy transfer and dopant proximity. Thin films of approximately 10 nm are synthesized by sequential radical-enhanced ALD of Y_2O_3, Er_2O_3, Yb_2O_3, and Eu_2O_3 at about 350°C. The composition, microstructure, cation distribution, local chemical bonding and optical properties of the as-synthesized thin films were determined by x-ray photoelectron spectroscopy, electron microscopy and photoluminescence measurements. To optimize the effect of the sensitizer and minimize the concentration quenching, the concentration and spatial distance between Yb^{3+}/Eu^{3+} sensitizers and Er^{3+} were controlled by changing the global deposition cycle sequence. Extended x-ray absorption fine structure analysis verified the spatial control of dopants in the Y_2O_3 host. It was found that multi-dopant spatial control allows for incorporation of minimal active sensitization sites, allowing for the possibility of maximizing the active Er concentration while maintaining efficient energy transfer. This additional degree of control allows for a class of complex materials that can potentially outperform their conventional counterparts by many-folds in luminescence.

5:40pm **TF2-TuA12 ALD of La Stabilized Amorphous HfO_2 High-k Dielectric Thin Films**, ***T. Wang***, *J.G. Ekerdt*, University of Texas at Austin

La_2O_3 was incorporated into hafnium dioxide grown by atomic layer deposition (ALD) to stabilize the amorphous phase during high temperature annealing. The incorporation was achieved by depositing HfO_2 and La_2O_3 alternatively in different ALD cycles. X-ray photoelectron spectroscopy compositional analysis shows that the Hf and La atomic percentage ratio can be controlled by varying the number of separate Hf and La ALD cycles. Microstructure was determined with X-ray diffraction and cross-sectional transmission electron microscopy. The introduction of La increases the film crystallization temperature from 5 00 °C for a HfO_2 film to 800 °C, 900 °C and 950 °C for 10 nm films containing 13% La (metal basis), 25% La and 43% La, respectively. Due to the ALD growth mechanism, the film is a HfO_2-$HfLa_xO_y$ periodic structure in which La just interacts with a limited thickness of HfO_2, and La-free layers mainly composed of HfO_2. The presence of periodic HfO_2 thin interval layers adds an extra advantage in amorphous stabilization during high temperature annealing over that found for homogeneous $HfLa_xO_y$ mixtures and less overall La is required. Therefore ALD incorporating La is a potential method to grow amorphous HfO_2-La_2O_3 high-κ dielectric thin films.

Tribology Focus Topic
Room: B2 - Session TR+SS-TuA

Surface Science for Tribology
Moderator: I. Szlufarska, University of Wisconsin, Madison

2:00pm **TR+SS-TuA1 Effect of the Surrounding Gas Pressure on Charge Separation Caused by Friction between Insulators**, ***T. Miura***, *E. Hosobuchi, S. Ueno, I. Arakawa*, Gakushuin University, Japan

Friction between insulators induces charge separation at the interface. The surface electrification after sliding contact yields electric field in the gap near the contact and results in gas discharge if the friction is carried out in a gas ambience. This gas discharge reduces the charge that was once induced at the frictional interface. It has been believed that the initial charge separation was not affected by a surrounding gas and was determined solely by the frictional materials. We have investigated the charge separation rate before the gas discharge under various gas conditions and found that it linearly decreased with the logarithm of the pressure from 10 Pa to atmospheric pressure for Ne, Ar, and Kr.

The friction experiment was performed by means of pin-on-disk equipment. The pin was made of natural diamond and was gold coated. The disk was quartz or sapphire. The charge accumulated on the gold-coated pin was measured by an electrometer. The diameter of a contact area between the bare diamond tip and the disk was about 10 μm and the sliding velocity was 11 μm/s. The charge on the pin increased at a constant rate during sliding and fell to zero when the gas discharge occurred. The charge accumulation and the gas discharge were repeated during sliding friction in a gas ambience. The initial charge density at the interface of the sliding contact was calculated from the accumulation rate, the track width and the sliding velocity.

The charge density was typically the order of 1 mC/m^2 for sliding friction in a vacuum (10 Pa). It was found that the initial charge separation under the atmospheric gas pressure is one order of magnitude smaller than that at 10 Pa. This reduction of the charge separation rate was observed for Ne, Ar, and Kr gas at almost the same efficiency. It is likely that the gas molecules penetrate into the frictional interface and interrupt or relax the charge separation. It should be necessary to investigate the surrounding gas effect on the initial charge separation in detail in order to reveal the origin of triboelectricity.

2:20pm **TR+SS-TuA2 *In situ* Tribology of Metal-Doped MoS_2: Interfacial Film Mechanics and Friction Behavior**, ***K.J. Wahl***, Naval Research Laboratory, *S.D. Dvorak,* University of Maine*, G.Y. Lee, I.L. Singer*, Naval Research Laboratory

Tribological processes that influence friction and wear involve a complex combination of materials science, physics, chemistry, and rheology. Our understanding of these sliding contact phenomena is limited by the fact that all the action takes place in a buried interface. Most often the only evaluation of these interfaces is accomplished through *ex situ* means after separating the contacts. *In situ* approaches to studying friction and wear processes are challenging because most engineering surfaces are metals or ceramics that have no optical transparency at visible wavelengths. For this reason, most of what is known about interfacial processes occurring during sliding has been learned through optical probes of sliding interfaces.

We have used an *in situ* tribometer to perform reciprocating sliding tests of Pb-Mo-S and Ti-Mo-S solid lubricant coatings. Experiments were performed in dry and ambient air. The interfacial films formed during sliding were monitored with *in situ* Raman spectroscopy and optical microscopy through transparent counterfaces. The dominant velocity accommodation mode in both dry and humid conditions was interfacial sliding between the surface of the wear track and the outer surface of the transfer film on the counterbody. Humid air sliding resulted in a second velocity accommodation mode involving shear and/or extrusion of the transfer film. We will demonstrate and discuss how the interface properties – shear strength and transfer film mechanical properties – affect friction behavior of these solid lubricant coatings.

2:40pm **TR+SS-TuA3 Nanosecond X-Ray Pulses From Peeling Tape in Vacuum**, ***S. Putterman***, *J.V. Escobar, C.B. Camara, J. Hird*, University of California, Los Angeles **INVITED**

That the surface between two interacting bodies can be a source of visible light –triboluminescence- has been known for centuries. Observation of the emission of nanosecond long 100.mW pulses of X-Ray photons from peeling tape indicates that tribological processes reach energy densities which are much greater than the few eV per molecule needed to generate visible photons. Analysis of the x-ray pulses indicates that they originate from micron scale regions near the vertex of peeling tape. Based upon this insight we are building a mechanically operated sub-millimeter x-ray source that can be used for medical imaging. The organized processes which transduce diffuse mechanical energy into x-ray pulses are not understood.

4:00pm **TR+SS-TuA7 Nanotribology at Cryogenic Temperatures**, ***S.S. Perry***, *X. Zhao, S.R. Phillpot, G. Sawyer, S.B. Sinnott*, University of Florida

The temperature dependence of the kinetic friction between a silicon nitride probe tip and a number of crystalline surfaces has been evaluated through atomic force microscopy measurements performed under an ultrahigh vacuum environment over the temperature range 140-750 K. Surfaces interrogated include highly oriented pyrolytic graphite, molybdenum disulfide, and lead sulfide. A relatively weak dependence on temperature is observed in the friction measured between 300 K and 750 K. As temperature decreases below ambient temperatures, a sharp increase in friction is observed for all surfaces, however with variations in the temperature threshold. Collectively, these results obtained from fundamental interfaces are consistent with an activated mechanism of energy dissipation during sliding. An Arhennius analysis of the temperature dependent friction over this range yields different effective activation energies, ranging from 0.1-0.4 eV for the thermally activated stick-slip motion of the probe tip on this surface. As temperature is reduced further, a distinct transition to a largely athermal behavior is detected and is shown to result from the onset of interfacial wear, entailing an alternative energy dissipation pathway.

4:20pm **TR+SS-TuA8 Molecular Dynamics Simulations of Nanoindentation of Si/SiO$_2$ Systems using the Charge Optimized Many-Body (COMB) Potential**, ***T.R. Shan***, *B. Devine, S.R. Phillpot, S.B. Sinnott*, University of Florida

Oxides and carbides, such as SiO$_2$, Al$_2$O$_3$, HfO$_2$ and SiC, are widely used together with Si in many high-performance electronic devices, including metal-oxide-semiconductor (MOS) devices/junctions and gate stacks. The lack of precise control over mechanical properties can lead to the degradation of these materials. It is therefore critical to understand the nanometer-scale mechanical properties of materials or complex systems being considered for use in electronic devices. Since nanoindentation has been established as a primary tool for investigating the mechanical behavior of small volumes of materials, classical molecular dynamics simulation is used to examine the nanoindentation of Si/SiO$_2$ interfacial systems. Because these systems consist of heterogeneous interface with significant changes in bonding as one crosses from one side of the interface to the other, the empirical charge optimized many-body (COMB) potential is used to model the structural evolution, mechanical response and charge transfer of Si/SiO$_2$ interfacial systems under the influence of a nanometer-scale indenter. The COMB potential allows for dynamic charge transfer between atoms and across interfaces, and does a good job in describing covalent and ionic bonding in these materials. Aspects of the Si/SiO$_2$ interface during nanoindentation, including dislocation formation and the mechanisms by which fracture occurs, will also be addressed. We gratefully acknowledge the support of the National Science Foundation through grant DMR-0426870.

4:40pm **TR+SS-TuA9 Influence of Molecular Structure and Alignment on Nanometer-Scale Tribology**, *P. Barry, P. Chiu, S.R. Phillpot,* ***S.B. Sinnott***, University of Florida

We report on the effect of small, fluorocarbon molecules on self-mated, aligned polytetrafluoroethylene (PTFE)-PTFE tribology using atomistic molecular dynamics simulations. Three fluorocarbon molecular classes were considered: C_2F_6, C_4F_{10} and C_8F_{18} with the amount of lubricant between the classes kept constant. Further, the effects of a relatively thin lubricating layer and a relatively thick lubricating layer were compared. The simulations predicted that the systems with thicker lubricating layers exhibited a friction coefficient that was significantly lower than those a thinner lubricating layer. Correspondingly, substantially more molecular wear of the PTFE surfaces were predicted for the latter systems. Interestingly, unlubricated PTFE-PTFE self-mated systems demonstrated low friction coefficients and molecular wear when the chains were slid in a direction parallel to the chain alignment, and unlubricated, aligned polyethylene (PE)-PE systems exhibited comparable or lower friction coefficients. The simulations further predicted that unlubricated, aligned PE-PTFE systems had friction coefficient values in between those of the PE-PE systems and PTFE-PTFE systems in which the chains slid in directions that were perpendicular to the alignment of the chains. Surprisingly, the highest friction coefficients in the PE-PTFE system occurred when the chains were slid in a direction parallel to the direction in which the chains were aligned. This result was attributed to the incommensurate nature of the sliding interface between the two different polymers. This work was carried out under the support of an AFOSR MURI.

5:00pm **TR+SS-TuA10 On the Mechanical Properties of Tungsten Disulfide Nanotubes**, ***I. Kaplan-Ashiri***, *S.R. Cohen, K. Gartsman*, Weizmann Institute of Science, Israel, *G. Seifert,* Technische Universität, Germany, *H.D. Wagner, R. Tenne*, Weizmann Institute of Science, Israel

WS$_2$ forms multiwalled nanotubes which seem to be almost defect free and their structure can be precisely defined. Hence they can serve as good candidates for the study of nanomechanics.

Various mechanical tests were applied on individual WS$_2$ nanotubes to reveal their mechanical properties and behavior. First, nanotubes were axially compressed in atomic force microscope, and their Young's modulus was observed according to Euler's buckling point. An average value of 170GPa was obtained. A similar test which was conducted in the scanning electron microscope resulted in large elastic deformation of the nanotube. Here the Young's modulus was obtained from the post buckling equations, and found to be 150GPa. In a third experiment, the nanotubes were axially strained until fracture occurred. The Young's modulus was then observed according to Hooke's law and found to be 152GPa. These moduli values are in good agreement between themselves and also with density functional tight-binding (DFTB) calculations and the bulk material (150GPa).

Tensile strengths and strain values as high as 16GPa and 14% were observed as well. These values reveal that WS$_2$ nanotubes reached their theoretical strength, hence they are suspected to be defect free. The high strain value is unique to the tubular nanophase of WS$_2$ and is also in good agreement with molecular dynamics simulation of MoS$_2$ nanotubes. The nanotubes were deformed elastically until failure, in "sword in a sheath" mechanism and probably fractured in a brittle mode.

Clamped nanotubes were bent and the shear (sliding) modulus was obtained according to Timoshenko's bending equation and found to be 2GPa. This value is in good agreement with DFTB calculations (4GPa) for sliding of two adjacent layers of MoS$_2$.

Furthermore, a unique nonlinear elastic deformation was observed both in post buckling and in bending tests. This mode of deformation is associated with the tubular structure.

5:20pm **TR+SS-TuA11 Nanotribological Characterization of Various Skin Cream Ingredients using Atomic Force Microscopy**, ***W. Tang***, *B. Bhushan,* The Ohio State University, *S. Ge*, China University of Mining and Technology

Skin cream is used to improve skin health and create a smooth, soft, pliable, and moist perception by altering the surface friction, adhesion, elastic modulus, and surface potential of the skin surface. As the industry continually searches for better cream formulations, it becomes increasing necessary to study how different cream ingredients interact with skin surface on the nanoscale. In this paper, vaseline, glycerin, and lanolin oil, which are the widely used ingredients in moisture cream, as well as the common moisture cream, advanced moisture cream, and oil-free moisture cream, were studied using an atomic force microscope (AFM). The binding interaction between skin cream and skin surface is one of the important factors in determining cream thickness and consequently the proper performance of skin cream. Film thickness, adhesive force and effective Young's modulus of various cream treated skin was measured using the force calibration plot technique with the AFM. Skin goes through various daily activities with time and the durability properties are closely tied to product performance. The durability of various skin creams were studied by repeated cycling tests. The health and feel of skin are significantly affected by its surface charging and the surface potential of virgin skin, and various cream treated skin was measured to determine the effects of various skin cream using the Kelvin probe method with the AFM. Relevant mechanisms are discussed.

5:40pm **TR+SS-TuA12 An Imaging TOF-SIMS Study of the Tribochemical Interactions in Diamondlike Carbon Films**, ***A. Erdemir***, *O. Eryilmaz*, Argonne National Laboratory

Diamondlike carbon (DLC) films combine many attractive properties which make them good prospect for a wide range of engineering applications. Depending on the sources of carbon (i.e., hydrocarbon gases or solid carbon or graphite targets) and the type of deposition method, some of the DLC films may contain large amounts of hydrogen in their structures and they are relatively soft. Those that are produced from solid carbon and/or graphite targets by arc-PVD and pulsed laser deposition are nearly hydrogen free but very hard. However, regardless of their chemical and/or structural nature, all DLC films tend to be very sensitive toward the chemical composition of the test environments when tested for their friction and wear properties. In this study, we concentrate our attention on the friction and wear behaviors of both the hydrogenated and hydrogen-free DLC films in the presence of inert and reactive gaseous species like, argon, oxygen, hydrogen, and deuterium in test chambers. Using time-of-flight secondary electron mass spectrometry (TOF-SIMS), we explore the extent of tribochemical interactions that occurred during sliding tests. These studies have confirmed that the friction and wear behaviors of DLC films are indeed very closely controlled by the type and extent of tribochemical events that are triggered by the gaseous species in the surrounding atmosphere. In particular, hydrogen and deuterium in test environments seems to interact with the sliding surfaces of these films and thus have the greatest effect on friction and wear. Inert gases were detrimental for the friction and wear behaviors of hydrogen-free DLC, but beneficial to that of the highly hydrogenated DLC films. Based on the results from TOF-SIMS studies, we provide a mechanistic explanation for the tribochemistry of sliding surfaces and correlate these findings with the friction and wear behaviors of DLC films.

Applied Surface Science
Room: Hall 3 - Session AS-TuP

Applied Surface Science Poster Session

AS-TuP1 XPS Characterisation of Thiol-SAMs on Au Surfaces for Biological Applications, *V. Trouillet,* Forschungszentrum Karlsruhe GmbH, Germany*, S. Engin, D. Wedlich,* University of Karlsruhe, Germany*, P. Mack, R.G. White,* Thermo Fisher Scientific, UK*, **M. Bruns***, Forschungszentrum Karlsruhe GmbH, Germany

Structured and oriented immobilisation of biomolecules has become subject of great interest in recent years due to the expected diversity of applications, e.g. biosensors in diagnosis, lab-on-chip technology, and modern cell culture focused on cell adhesion, migration, and differentiation. Therefore, a lot of effort has been spent to develop strategies for covalent and non-covalent immobilization of proteins, respectively. A very promising approach is surface patterning by micro-contact printing (µCP) to produce self-assembly-monolayers (SAMs) on gold surfaces based on mixtures of benzylguanine thiol (BGT) and matrix thiol. In this case BGT is the substrate for the SNAP-tag system, allowing for covalent attachment of any protein of interest fused to this tag, whereas the inert matrix thiol acts as spacer for BGT and moreover prevents from non-specific protein adsorption.

The present contribution focuses on surface analytical characterization of pure benzylguanine and matrix thiols as well as mixtures of both by means of X-ray photoelectron spectroscopy (XPS) to achieve information on chemical binding states in a non-destructive manner. For this purpose all SAMs were prepared on gold films deposited onto glass substrates by r.f. magnetron sputtering directly prior to the thiol exposure. In particular, XPS proves the covalent binding of the thiols and concentration depth profiles constructed from angle resolved data applying the maximum entropy method reveal the orientation of the SAMs together with thickness information. The µCP micro-structures were verified by small area XPS together with time-of-flight secondary mass spectrometry. In addition, scanning electron microscopy and ellipsometry were used to achieve a comprehensive characterization.

AS-TuP2 Dielectric Response of AlSb Determined by In-Situ Ellipsometry*, **Y.W. Jung**, T.H. Ghong, J.S. Byun, S. Kim, Y.H. Cha, Y.D. Kim,* Kyung Hee University, Korea*, H.J. Kim, Y.C. Chang,* Academia Sinica, Taiwan and University of Illinois at Urbana-Champaign*, S.H. Shin, J.D. Song*, Korea Institute of Science and Technology, Korea

We present pseudo dielectric function data $<\varepsilon> = <\varepsilon_1> + i<\varepsilon_2>$ from 0.7 to 5.0 eV of oxide-free AlSb at 300 K that is currently the most accurate representation of the bulk dielectric response ε of the material. The data were obtained by in-situ spectroscopic ellipsometry (SE). SE is a well-known method of obtaining $<\varepsilon>$ directly, without requiring Kramers-Kronig analysis. AlSb is an important material for optoelectronic applications such as infrared optical devices and high-electron-mobility transistors. However, because overlayers strongly affect $<\varepsilon>$ and Al reacts readily with oxygen, the approximate determination of ε of any Al-containing semiconductor ordinarily requires complex processing to minimize overlayer artifacts. We avoid this by using in situ SE to obtain $<\varepsilon>$ data before oxides have the opportunity to form.

Our measurements were done on an AlSb film d = 1.5 mm thick that was grown on a GaAs (001) substrate using molecular beam epitaxy (MBE). Since d is significantly larger than the critical thickness of AlSb, the film is fully relaxed and its measured dielectric properties closely approximate those of bulk material. The growth station features an integrated spectroscopic ellipsometer. Measurements were made through strain-free windows while maintaining the AlSb layer in ultrahigh vacuum. In the interference-oscillation region, ε was extracted with a multilayer parametric model. Compared to previously reported results, our $<\varepsilon_2>$ data show lower and higher values in the E_1 and E_2 spectral regions, respectively, confirming that our data are less affected by overlayers. We also observe the indirect band gap of AlSb, and obtain the E_0, $E_0 + \mathit{\Delta}_0$, E_1, $E_1 + \mathit{\Delta}_1$, E_0', $E_0' + \mathit{\Delta}_0'$, E_2, and $E_2 + \mathit{\Delta}_2$ critical-point (CP) energies from numerically calculated second derivatives. Band-structure calculations done using the linear augmented Slater-type orbital (LASTO) method were performed to identify overlapping CPs in the E_2 energy region. The calculated CP energies agree well with those obtained from data, confirming the validity of the calculations. Our results will be useful in various contexts, including the design of optoelectronic devices.

AS-TuP3 Crossing of the E_2, $E_2+\Delta_2$, E_2' and $E_2' + \Delta_2'$ CPs in $InAs_xSb_{1-x}$ Alloys as Determined by Spectroscopic Ellipsometry*, **J.J. Yoon**, T.J. Kim, S.Y. Hwang, Y.J. Kang,* Kyung Hee University, Korea*, D.E. Aspnes,* Kyung Hee University, Korea and North Carolina State University*, Y.D. Kim,* Kyung Hee University, Korea*, H.J. Kim, Y.C. Chang,* Academia Sinica, Taiwan and University of Illinois at Urbana-Champaign*, J.D. Song*, Korea Institute of Science and Technology, Korea

Owing to its small band gap, $Hg_xCd_{1-x}Te$ is the dominant material for infrared (IR) detectors. However, due to the high Hg vapor pressures needed during growth, accurate compositions x are difficult to obtain, particularly over large areas. The low-bandgap III-V ternary alloy $InAs_xSb_{1-x}$ exhibits important advantages, including better control of composition during growth, higher electron and hole mobilities, and the availability of high-quality, low-cost substrates. As a result, $InAs_xSb_{1-x}$ alloys have recently been used to fabricate various IR optoelectronic devices. Although the optical properties and main critical-point (CP) energies of the binary endpoints InAs and InSb are well known, much less information is available for alloys of arbitrary x. Here, we report pseudodielectric function $<\varepsilon> = <\varepsilon_1> + i<\varepsilon_2>$ data from 1.5 to 6.0 eV of $InAs_xSb_{1-x}$ alloys for selected values of x over the entire composition range, assessing the removal of overlayers in real time to ensure that overlayer artifacts are minimized and therefore, that the data most closely represent the intrinsic dielectric responses e of these materials. Energies of the E_1, $E_1 + \mathit{\Delta}_1$, E_0', $E_0' + \mathit{\Delta}_0'$, E_2, $E_2 + \mathit{\Delta}_2$, E_2', $E_2' + \mathit{\Delta}_2'$, and E_1' critical points (CPs) were obtained from numerically calculated second derivatives, and identified where necessary by band-structure calculations done using the linear augmented Slater-type orbital method (LASTO). The calculated CP energies agree well with those obtained from data, confirming the validity of the calculations. These calculations show a crossing of the E_2, $E_2 + \mathit{\Delta}_2$, E_2', and $E_2' + \mathit{\Delta}_2'$ CP structures with increasing As-composition. Also, the band-structure calculations allow us to identify the InSb structures at 3.31 and 3.75 eV with the $\mathit{\Delta}_5^{cu} - \mathit{\Delta}_5^{vu}$ and $\mathit{\Delta}_5^{cl} - \mathit{\Delta}_5^{vu}$ saddle points at $k = (0.35, 0, 0)$. These saddle points were reported previously only at low temperature. Our results will be useful in a number of contexts, including the design of optoelectronic devices based on InAsSb and obtaining a more detailed understanding of the band structure of these and related alloys.

AS-TuP4 Gold Nanodot Array on Silicon Fabricated by Scanning Probe Lithography, ***M, Kanda**, T. Ichii, K. Murase, H. Sugimura*, Kyoto University, Japan

Gold nanoobjects are recognized as important materials to construct the advanced nanoscale technology for electronic, optical, and sensor devices because they can transfer a near-field light between them in a well-aligned arrangement. The aligned arrangement of gold nanoobjects requires a preliminarily patterned substrate with the nanometer-scale precision. Scanning probe lithography (SPL) utilizing atomic force microscopy (AFM) is a very powerful technique to fabricate nanoscale patterns even under atmospheric condition.

In this study, a well-aligned array of gold nanodots was fabricated using SPL. A Si(111) surfaces covered with self-assembled monolayers (SAM) of 1-hexadecene (HD) were used as substrates. HD-SAMs have high chemical durability to hydrofluoric acid (HF) and were used as resist film of SPL. Nanoscale patterns of silicon oxides were fabricated by applying DC bias voltages between an AFM probe and the substrate. Since the HD-SAMs had a highly ordered structure and only 2.3 nm thicknesses, the size and the position of the oxides were precisely controlled. Then, the oxides were etched by immersing the samples into HF solution, and the underlying Si surfaces on the nanopatterns were exposed. After the HF etching, the samples were immersed into an Au electroless plating solution and gold nanodots were deposited only on the nanopatterns. The structures and the optical properties of the gold nanodots arrays were investigated by field emission scanning electron microscopy (FE-SEM) and spectrophotometer, respectively.

AS-TuP5 Ultrashort Pulse Laser Ablation as a Tool for the Depth Profiling of *Staphylococcus Epidermidis* Microbial Biofilms, ***S. Milasinovic**, M. Blaze, Y. Liu, Y. Zhao, J. Johnston, R.J. Gordon, L. Hanley*, University of Illinois at Chicago

Ultrashort pulse laser irradiation is known to cause minimal laser induced damage when interacting with soft biological materials and might therefore be used for depth profiling in mass spectrometric imaging. This work examines the possibility of using this technique for chemically non-destructive ablation of microbial biofilms. Biofilms of *Staphylococcus epidermidis* were grown on indium tin oxide coated glass slides. ~100 µm thick biofilms were obtained after 3 day incubation by the drip flow method. These biofilms were then irradiated with 45 fsec pulses of 800 nm radiation from a Ti-Sapphire laser. Effects of varying the laser fluence and numbers of pulses were investigated by focusing the laser beam to a ~200 µm spot diameter. Laser ablated craters were imaged by scanning electron microscopy and two-photon laser scanning microscopy. The ablation threshold was determined to be 0.08 J/cm^2. Biofilms were then spiked with Br-tyrosine, which was detected by laser desorption postionization mass spectrometry within the intact biofilms before and after laser ablation. Mass spectra obtained at different locations were compared to determine the extent of chemical damage done by laser irradiation.

AS-TuP6 Vacuum Ultraviolet Light Induced Chemical Modification of Cyclo-Olefin Polymer Surface Dependent of the Irradiation Atmosphere, *Y.J. Kim*, *H. Sugimura, K. Murase,* Kyoto University, Japan*, Y. Taniguchi, Y. Taguchi*, Alps Electric, Japan

In recent years, cyclo-olefin polymer (COP) resins have been used in a variety of applications owing to their excellent properties and low cost, and the market for cop resins is growing every year[1]. For improvement in adhesivity, dyeability, and wettability, extensive research to develop practical and economical methods for the surface modification of COP has been carried out by many groups. In particularly, wettability and adhesion are critical design features for many commercial products. For this purpose, corona discharge treatment, plasma etching, ultraviolet irradiation, and chemical solution etching have been employed. Although it is desirable to provide addition functions to polymer surfaces, it is also important to do so without affecting their bulk characteristics, such as mechanical, thermal, and other intrinsic properties. Ultraviolet irradiation should be the best method in this respect, since ultraviolet irradiation interacts only with the polymer surface and does not penetrate into the centre of the material. This study sought to photochemically convert the surface of COP into a hydrophilic surface consisting of oxygen functional groups such as C–O, C=O, and COO components by simple irradiation with a vacuum ultra-violet (VUV) light of 172 nm wavelength in the presence of atmospheric oxygen molecules. We found that this hydrophilic surface served as a base for the formation of adhesive chemical bonds at the interface to improve the wettability and adhesion properties. We have optimized the VUV photochemical conversion conditions for the COP surface[2].

In this study, we report how different the chemical nature of COP surfaces irradiated with the VUV light is, dependent on the VUV-irradiation atmosphere. The extent of oxygenation was evaluated by XPS and FTIR-ATR spectra, and it was shown that the surface properties, hydrophilicity, and functionalization were crucially dependent on the VUV irradiation atmosphere. Roles of oxygen, nitrogen and water molecules in the VUV-irradiation environment on the surface modification have been elucidated.

References

[1] M. Yamazaki, J. Mol. Catal. A: Chem. 213, 81 (2004)

[2] Y. J. Kim et al., Applied Surface Science 255, 3648 (2009)

AS-TuP7 Dynamic Solid-liquid Interaction on Hydrophilic Surfaces, *Y. Yokota*, *N. Yoshida,* The University of Tokyo, Japan*, M. Sakai,* Kanagawa Academy of Science and Technology, Japan*, A. Nakajima,* Tokyo Institute of Technology, Japan*, T. Watanabe*, The University of Tokyo, Japan

Dynamic solid-liquid interaction as a liquid droplet-movement on inclined hydrophilic~hydrophobic surfaces was investigated. The liquid droplet movement was affected by a surface energy, roughness, and homogeneity of the solid surface, and furthermore it is suggested that the internal fluidity detected by Particle Image Velocimetry method determined the rate. The movement also depended on the shape of a droplet, that possibly changed the internal flow drastically. In this presentation, we will discuss about the detail of relations among them.

AS-TuP8 Relationship between In-Depth Profiles and Local Structures in HfSiO Film Studied by Photoemission Spectroscopy and Extended X-Ray Absorption Fine Structure, *S. Toyoda*, The University of Tokyo, Japan*, H. Ohfuchi,* JASRI*, H. Kamada, M. Oshima,* The University of Tokyo, Japan*, G. Liu, Z. Liu, T. Sukegawa, K. Ikeda*, STARC

High dielectric (high-k) transition metal oxide materials such as ZrO2, HfO2, and their silicates are widely investigated to reduce the leakage current from channel to gate, because SiON gate dielectrics have reached a physical thickness scaling limit of complementary metal- oxide-semiconductor (CMOS) devices. Among them, HfSiO and nitrided HfSiO are promising candidates due to appropriate band gap, soft reactivity to the Si substrate, and suppression of crystallization. In this study, we have demonstrated annealing effects on in-depth profiles and local structures in the HfSiO films by angle-resolved photoemission spectroscopy and extended x-ray absorption spectroscopy. HfSiO films with thicknesses of 2.0 nm were deposited on 0.7 nm SiON interfacial layers using an atomic layer deposition (ALD) technique. Annealing was performed at 850 °C and 1050 °C for 1 min in a nitrogen gas of 1 atm by the direct current flowing method through the Si substrate. Photoemission measurements were performed at BL-2C of the Photon Factory in High Energy Accelerator Research Organization (KEK). The total energy resolutions were estimated to be 0.20 eV for photon energy of hv = 630 eV. Photoelectron emission angles were changed from the surface normal to 60° for enhancement of surface sensitivity. To analyze in-depth profiles from angle-resolved core-level photoemission spectra measured by tilting the samples, the maximum entropy method, which was coded according to previous reports, was utilized. The validity of the in-depth profiles was confirmed by comparison with Rutherford backscattering spectroscopy (RBS). In-depth profile of the HfSiO film presents a complicated layer structure even at the as-grown stage; Si concentrations are high in both surface and interface regions and nitrogen atoms are slightly distributed at the interfacial layer. Accumulation of Si atoms at the surface is known by the ALD growth and the in-depth profile in the as- grown sample is quantitatively confirmed by RBS measurements. It should be noted that changes in the in-depth profiles suggest that Si oxide components diffuse from the interfacial SiOxNy layer into the HfSiO layer and concentrations of Hf relatively decrease. Coordination number obtained by Fourier transform of the EXAFS spectra decreases with increasing annealing temperature, suggesting that chemical bonding states on nearest neighbor of the Hf atoms in the HfSiO layer change with Si diffusion due to oxidation of the Si substrate.

AS-TuP9 In Situ XPS Depth-Profiling of Hydrogen Storage Material VCrTi during Thermal Annealing, *J.R. Harries*, *Y. Teraoka, A. Yoshigoe, M. Tode*, Japan Atomic Energy Agency

VCrTi is a candidate material for hydrogen-storage. The presence of a surface oxide layer, its thickness, and its composition can be expected to effect the properties of charging and release of stored hydrogen, and as such it is of interest to characterise the native oxide, and to investigate whether more desirable properties can be obtained by artificially modifying the surface composition. In this study we have used synchrotron radiation photoelectron spectroscopy to study the chemical composition of the native oxide layer of a commercial sample of $V_{25}Cr_{40}Ti_{35}$ alloy. The total XPS energy resolution is sufficient to provide chemical state-specific information, and spectra recorded at a range of different take-off angles provide information on the depth-profiles of the composition. The maximum entropy method is used to generate element-specific (and chemical state-specific) depth profiles from the spectra. The following conclusions are drawn:-

The thickness of the native oxide layer as determined from the XPS data is consistent with a TEM analysis, at approximately 5 nm, and consists of oxides of vanadium, chromium, and titanium, in amounts roughly corresponding to the composition of the alloy. It also contains carbon. Depth-profiling suggests that the carbon forms a sub-layer.

Thermal annealing gradually reduces the oxide coverage with increasing temperature. After heating to 800 degrees C, the dominant surface component appears to be titanium oxides, with vanadium and chromium oxides only remaining below the surface.

It is also planned to study the chemical composition of a sample irradiated with hydrogen (deuterium) ions, and study the uptake of hydrogen for samples with oxide layers of differing composition.

AS-TuP10 Automated XPS Analysis of Passivated Stainless Steel to the SEMI Standard, *T.S. Nunney*, *O. Mustonen, J. Wostenholme,* Thermo Fisher Scientific, UK*, B.R. Strohmeier, J.D. Piasecki, R.J. Lee*, RJ Lee Group, Inc.

The Semiconductor Equipment Manufacturers Institute (SEMI) defines methods for analysing the elemental composition and metallurgical characteristics of metal used in components for high purity gas distribution systems. Typically stainless steel components are treated to improve surface quality and prolong their lifetime and performance. In the passivation process a chromium-rich ‘passive’ layer is formed on top of the steel surface. The SEMI procedures define methods to determine the surface and oxide composition and chemistry of the interior surface of chromium enhanced stainless steel tubing. The key metrics that are used to identify passivated steel are the total Cr/Fe surface atomic ratio, the Cr oxide/Fe oxide surface atomic ratio, and the total oxide thickness.

The current SEMI test methods have been used since 1992 (former SEMASPEC methods) and use both X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) to evaluate the passivation of the stainless steel surface. Since then XPS instrumentation has developed significantly which enables the determination of the parameters quickly and easily with XPS only. This work describes how the test procedure can be automated from start to finish with combination of modern XPS instrumentation and software. In particular, procedures can be used to maintain consistency of approach in the important peak-fitting steps to eliminate inconsistencies which can be introduced by different users. The automated approach can be extended to include sputter depth profiling of the passivation layer, resulting in a method for batch control or failure analysis of a series of samples.

AS-TuP11 Vacuum Annealing Phenomena in Ultrathin TiDy/Pd Bi-Layer Films Evaporated on Si(100) as Studied by TEM and XPS, ***E.G. Keim***, University of Twente, The Netherlands, *W. Lisowski*, Polish Academy of Sciences, Poland

Using a combination of TEM and XPS, we made an analysis of the complex high-temperature annealing effect on ultra-thin titanium deuteride (TiD_y) films evaporated on a Si(100) substrate and covered by an ultra-thin Pd layer. Annealing induced deuterium evolution from such material[1] can be applied as a useful source of deuterium used in chemical and energetic reactions. In this report we show to what extent structural changes occur within the ultrathin Si/TiDy/Pd film area as a result of annealing. The TEM/XPS data are compared for two films, one taken before, the second after annealing. 10 - 20 nm thick TiD_y films on a Si substrate each covered by 10 - 20 nm thick Pd were prepared in a UHV glass system[2]. Mass spectrometry was used to monitor in situ deuterium evolution from the film during annealing, all other analyses were performed ex situ. It was found that the $Si/TiD_y/Pd$ assembly undergoes a microstructural and chemical conversion as a result of annealing. Energy Filtered TEM (EFTEM) mapping of cross-section images and XPS depth profiling analysis revealed both a broad intermixing between the Ti and Pd layers and an extensive inter-diffusion of Si from the substrate into the film bulk area. Selected Area Diffraction (SAD) reveals very fine crystallites of $PdTi_2$ and the initial stages of TiSi phase formation. Segregation of Ti towards the Pd top layer surface has been evidenced using Angle Resolved XPS (ARXPS) and the EFTEM image analysis.

References

[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).

AS-TuP13 Investigation of Metal-Assisted SIMS and Cluster Ion Bombardment for Analysis of Polystyrene Surfaces, ***H.F. Arlinghaus***, *F. Lipinsky,* Westfälische Wilhelms-Universität Münster, Germany, *N. Wehbe, A. Delcorte, P. Bertrand,* Université Catholique de Louvain, Belgium, *L. Hoissiau,* University of Namur, Belgium, *A. Heile*, Westfälische Wilhelms-Universität Münster, Germany

In addition to structural information, a good knowledge of the local chemistry proves to be of ever greater importance for the development of new types of materials as well as for specific modifications of interfaces and surfaces. A detailed understanding of the systems is required in multiple fields of the metal and semiconductor industries and for various biomedical and chemical applications. In particular, the ongoing miniaturization and the associated reduction of the volumes of material available for analysis constitute a challenge for the detection limits of quite a number of characterization techniques.

In the case of TOF-SIMS, several methods of secondary ion yield enhancement have been proposed. Our contribution focuses on two of these methods, i.e. metal-assisted SIMS and polyatomic primary ion bombardment (e.g. Bi_3^+, C_{60}^+). In previous studies on thicker layers of organic molecules it was found that polyatomic primary ions generally increase the secondary ion yields and that a yield enhancement due to gold deposition can only be detected for monoatomic ion bombardment [1,2]. To investigate advantages and drawbacks of the use of MetA-SIMS and polyatomic primary ion bombardment in more detail, not only thicker layers of several ten nanometers but also layers of only some nanometers thickness of polystyrene were prepared. The samples, pristine and metallized with different amounts of gold, were analyzed using monoatomic and polyatomic primary ions.

[1] A. Heile, D. Lipinsky, N. Wehbe, A. Delcorte, P. Bertrand, A. Felten, L. Houssiau, J.J. Pireaux, R. De Mondt, P. Van Royen, L. Van Vaeck, H. F. Arlinghaus, Surf. Interface Anal. 40 (2008) 538-542, doi:10.1002/sia.2810.

[2] N. Wehbe, A. Heile, H.F. Arlinghaus, P. Bertrand, A. Delcorte, Anal. Chem. 80 (2008), 6235-6244, doi: 10.1021/ac800568y

AS-TuP14 Surface Analysis of Electro-Polished Niobium Cavity-Samples for RF Applications, ***P.V. Tyagi***, *M. Nishiwaki, T. Saeki, M. Sawabe, H. Hayano,* KEK, Japan, *T. Noguchi,* KAKEN Inc., Japan, *S. Kato*, KEK, Japan

The performance of superconducting RF cavities is restricted by the contaminations present on the surface and the surface roughness. In the recent years extensive research has been done to enhance the cavity performance by applying improved surface treatments such as mechanical grinding (MG), electro-polishing (EP), chemical polishing (CP), tumbling, etc followed by various post-treatment methods like ultrasonic pure water rinse, alcoholic rinse, high pressure water rinse, hydrogen per oxide rinse etc. Although EP post-treated by various methods has revealed good results to obtain smooth and clean surface, still more research and efforts are required in this area. Prior XPS (x-ray photoelectron spectroscopy) analysis of EPed Nb samples demonstrate that the surface was covered mainly with the niobium oxide (Nb_2O_5) along with carbon in addition, a small quantity of sulfur and fluorine was also found in SIMS (secondary ion mass spectroscopy) analysis even they were post-treated by various methods. In this article we present the analysis of surface contaminations and roughness for a series of EPed Nb samples located at various positions of a single cell Nb cavity followed by post-treatment methods and our endeavor to understand the performance of EP in a cavity with the help of surface analytical tools like XPS, SIMS and SEM (scanning electron microscope) at KEK.

AS-TuP15 Kelvin Probe Force Microscopy on Phase-Separated Self-Assembled Monolayers of Alkanethiol and Amide-Containing Alkanethiol, ***S. Ikebukuro***, Kyoto University, Japan

Frequency modulation atomic force microscopy (FM-AFM) is a very powerful tool for investigating various materials including organic samples. Since the chemical interaction and the van der Waals interaction between the tip and the sample are the main origin of the FM-AFM contrast, it can be applied for chemical identification of surface functional groups as well as structural analysis of organic ultrathin films[1, 2]. However, the decay-length of those interaction is less than 1 nm, the FM-AFM contrast only provides the chemical information of the sample surface and the subsurface information is difficult to be obtained. On the other hand, Kelvin probe force microscopy (KFM) is a method to investigate surface potential (SP) distribution on the nanometer scale. Since the electrostatic force, which is the origin of KFM contrast, is a long-range interaction, it is expected that we can obtain the subsurface information and discriminate two separated areas that have same surface profile while subsurface structures differ from each other using KFM.

In this study, to evaluate transitions of SP caused by the difference of subsurface structures, we investigated a phase-separated self-assembled monolayer (SAM) formed from a binary mixture of nearly isometric adsorbates, n-alkanethiol (n-dodecanethiol : DDT) and amide-containing alkanethiol (3-mercapto-N-octylpropionamide : 1ATC8), on a Au(111) substrate using FM-AFM/KFM. The SAMs were prepared by the coadsorption from an equimolar solution of DDT and 1ATC8 (1 μM in total thiol) and two separated regions were discriminated in the FM-AFM/KFM images. The same experiments were also performed on a DT/1ATC8 phase separated SAMs. We compared these results and concluded that the SP of the 1ATC8 areas was lower by 240 mV compared to the DDT areas. Considering the differences of molecular properties between DDT and 1ATC8, these SP images present reasonable contrast and suggest that the difference of the subsurface structures was detected using FM-AFM/KFM.

References

[1] T. Ichii et al., Jpn. J. Appl. Phys. 43, 4545 (2004)

[2] T. Ichii et al., Jpn. J. Appl. Phys. 44, 5378 (2005)

AS-TuP16 Surface Potential Measurement of Organo-Chalcogenide Self-Assembled Monolayers using Kelvin Probe Force Microscopy, ***T. Ichii***, *S. Nanjo, S. Ikebukuro, K, Miki, K. Murase, K. Ohe, H. Sugimura*, Kyoto University, Japan

Organo-chalcogenides (sulfide, selenide, and telluride) have been expected to play an important roll in molecular electronics because they can be bound onto noble metals. Functional groups with the chalcogene atoms in these molecules act as anchoring groups, and the molecule-metal bindings can be modified by changing the atom species. Some of the organo-chalcogenides are formed into self-assembled monolayers (SAMs) and they have been intensively studied as model structures of molecule-metal binding.

Kelvin probe force microscopy (KFM), which is one of scanning probe techniques, is an outstanding method for the investigation of local surface potential on the nanometer scale. Since surface potential of organic monolayers on substrates reflects dipole moment of the organic molecules and interfacial dipole moment between the molecules and the substrate, KFM allows us to clarify how the anchoring groups effect on electric properties of the molecule-metal bindings.

In this study, we investigated surface potential distribution of phase-separated SAMs composed of organosulfide and organoselenide using KFM. Dibenzyl-disulfied (BS), dibenzyl-diselenide (BSe) and 3-mercapto-N-octylpropioneamide (1ATC8) were used and phase-separated SAMs of BS/1ATC8 and those of BSe/1ATC8 were prepared. The 1ATC8 areas in the SAMs were used as a reference in the surface potential measurement. The surface potential of the BSe area were higher by approximately 300 mV compared to the BS regions and we concluded that it was mainly due to the difference of the interfacial dipole moment.

AS-TuP17 Lattices of Freestanding Carbon Nanofibres Characterized by Spectroscopic Ellipsometry

R. Magnusson, Linköping University, Sweden, *R. Rehammar,* Göteborg University, Sweden, *H. Arwin*, Linköping University, Sweden

Photonic crystals with lattice constant in the visible range of light can be fabricated using freestanding carbon nanofibres. These types of structures are optically complicated, with geometric effects both from the lattice and from individual scatterers. In this report, results from pilot studies of the optical properties of such samples are presented.

Ellipsometric measurements on samples with vertically aligned arrays of free-standing carbon nanofibres with lengths up to 1600 nm are presented. The carbon nanofibres were grown on silicon wafers with a 70 nm layer of titanium and a 15 nm layer of titanium nitride using plasma-CVD with nickel as catalyst. Electron beam lithography was used to create the nanofibre lattice. Samples with varying periodicity and length of the carbon fibers, i.e. film thickness, were investigated.

In this pilot study measurements were performed with a dual rotating compensator ellipsometer in the spectral range 245-1700 nm. The instrument provides the full Mueller matrix of the sample and measurements were performed at multiple angles of incidence and different sample orientations.

The samples show no difference in the optical response when rotated 90°, but at other orientations changes in the spectrum are observed below a wavelength of approximately 1000 nm. The analysis of the ellipsometric data is presented and different modeling approaches are discussed.

AS-TuP19 Spectroscopic Ellipsometry of Bulk MAX-phases

A. Mendoza-Galvan, Cinvestav-Queretaro, Mexico, *M. Rybka, K. Järrendahl, H. Arwin, M. Magnuson, L. Hultman,* Linköping University, Sweden, *M. Barsoum*, Drexel University

MAX-phases are compounds with the chemical formula $M_{n+1}AX_n$ where M is a transition metal, A is an element from column 13 to 16 in the periodic system and X represents C or N and n = 1, 2 or 3. These materials are potentially technologically important as they show unique refractory and other physical properties due to the combination of metals and ceramics. From a fundamental point of view the band structure of these materials are of interest and optical reference data are important to determine. Herein we report, for the first time, on the optical properties of NbTiAlC, Nb_2AlC, $TiSC_2$, Cr_2GeC, $TiGeC_2$, Ti_2AlC, and Ti2AlN by spectroscopic ellipsometry in the 0.03 to 6.0 eV spectral range. The ellipsometric data in the infrared range show features corresponding to Fano modes indicating the presence of a thin oxide layer a few nm thick. The optical response of these MAX-phases is represented by a Drude-Lorentz model. Thus, in the low energy range the electrical conductivity through the Drude term is evaluated and two or three interband electronic transitions which are compositional dependent can be identified at photon energies in the visible-ultraviolet range 1.0-6.0 eV.

AS-TuP20 In-Situ Synperonic Film Growth on Self Assembled Monolayers and Organic Polymers Investigation Using Quartz Crystal Microbalance in Conjunction with Spectroscopic Ellipsometry

A. Kjerstad, *T. Hofman, E. Schubert, M. Schubert*, University of Nebraska - Lincoln

Thin film growth in an aqueous environment of a high water content film is difficult to characterize due to the ambient conditions and unknown porosity of the film. We report on the investigation of aqueous in-situ synperonic thin films. These films are grown on self-assembled monolayers and organic polymers of varying hydrophobicities. The deposition is measured using quartz crystal microbalance (QCM) in conjunction with spectroscopic ellipsometry (SE). The strength of QCM lies in it's ability to determine the mass of deposition, whereas SE is highly sensitive to changes of index of refraction and film thickness. These findings are used to model film deposition and behavior. The models are created using two instrumentation techniques, thus ensuring validity.

AS-TuP21 Ellipsometric Study of Ga-Doped ZnO Films Deposited on Large Area Substrates by Pulsed Laser Deposition

D. Agresta, *K. Leedy, B. Bayraktaroglu*, U.S. Air Force Research Laboratory

Transparent conductive Ga-doped ZnO (GZO) thin films are prepared on large-area substrates by pulsed laser deposition (PLD) for optoelectronic contact applications. Limited reports exist of large area PLD of oxide thin films. A previous study of Al-doped ZnO (AZO) films reported high quality material being obtained over large areas by using a combination of off-axis PLD and post deposition annealing at 400°C in forming gas [1]. This paper utilizes these same techniques for the fabrication of GZO (3% Ga_2O_3) on Si or quartz substrates up to 100 mm in diameter. We report on the effect of different PLD temperatures (400, 500, and 600°C) and pressures (5, 10, 50 mTorr) on the uniformity and stability of pre- and post-annealed GZO film properties.

The optical properties (refractive indices, absorption coefficients, and energy gaps) of the GZO thin films are extracted primarily by spectroscopic ellipsometry (SE). SE has been used to determine the optical functions of ZnO films. Known for its precision and non-destructiveness, SE is an indirect measurement technique in the sense that the film properties of interest are obtained by a nonlinear regression analysis of measured data to an optical model. This enables the extraction of both the real and imaginary parts of the dielectric function, without directly involving Kramers–Kronig analysis, while simultaneously determining the film thickness with great precision. SE spectra are obtained with a Horiba Jobin Yvon UVISEL spectroscopic ellipsometer from 0.6 to 4.7 eV and analyzed with the self-contained DeltaPsi2 (DP2) software package. Additionally, we present comparative studies using normal incidence reflectance and transmission, atomic force microscopy (AFM), optical interferometry, x-ray diffraction (XRD), and scanning electron microscopy (SEM) which will either confirm the ellipsometric optical model or may reveal parameters for their incorporation. Lastly, the electrical properties are considered by resistivity measurements.

Reference:

1. K. D. Leedy, C. V. Varanasi, D. H. Tomich and B. Bayraktaroglu, "Al-doped ZnO Thin Films Deposited on Large-area (100 mm Diameter) Substrates using Pulsed Laser Deposition for Optoelectronic Contact Applications," 5th International Workshop on ZnO and Related Material (2008).

AS-TuP22 The Optimized Wet Cleaning for Extreme Ultraviolet (EUV) Masks: Cleaning Efficiency for Residual Photoresist and Ru Capping Layer Surface

H. Seo, *J.Y. Park,* University of California, Berkeley and Lawrence Berkeley National Laboratory, *T. Liang,* Intel Corporation, *G.A. Somorjai*, University of California, Berkeley and Lawrence Berkeley National Laboratory

Extreme Ultraviolet (EUV) lithography is a leading technology for future top-down semiconductor device manufacturing. Since this technology relies on the beam projection by reflection, Mo-Si multilayer (ML) stacks are used for EUV masks, to maximize the reflection from the mask. It is challenging and necessary to effectively remove contaminants from the masks and mirrors without adverse effects on their surfaces. Furthermore, process-induced contaminations on mask surfaces such as residual photoresist, metalorganic compounds, and sub-micron particles during patterning, handling, and use of EUV masks also affect the ML surfaces and cause problems for resist print on the wafer. Thus, the development of an effective cleaning process is one of critical technical issues, which must be resolved in order to achieve damage-free, efficient, and reliable cleaning methods for use in EUV lithography.

In this study, the efficiency of various wet cleaning methods for EUV mask blanks were investigated using surface sensitive characterization techniques. Two types of samples were prepared for cleaning: (i) EUV mirrors capped with 3 and 6 nm Ru layer on Mo-Si multilayers and (ii) e-beam photoresist (PR) coated Ru layer on Mo-Si multilayers. These two types of samples were cleaned using various wet chemicals to evaluate both the cleaning efficiency for resist and organic contaminants and the chemical effects on the Ru surfaces. The wet chemicals used in the study include tetramethyl ammonium hydroxide (TMAH), non-toxic organic solvents and sulfuric acid. The chemical compositions of the EUV mask blanks were characterized with x-ray photoelectron spectroscopy (XPS) before and after each cleaning process. Atomic force microscopy (AFM) and Scanning Electron Microscope (SEM) were used to investigate the influence of cleaning methods on the surface morphology and roughness. The chemical analysis of the EUV masks after these treatments revealed different chemical effects on the Ru oxidation state and surface carbon concentration depending on the pH of the wet solution. A surface reaction model for the behavior of Ru and RuO_2 in wet solutions is proposed. More importantly, the systematic study to seek optimized chemical solutions for efficient residual PR removal and improved EUV mask surface reflectivity was carried out and the results are presented and discussed.

AS-TuP23 XPS and RBS Quantification of Pulsed Laser Deposition of LAO/STO Heterostructures: Unexpected Variations in Stoichiometry

M.H. Engelhard, *T. Droubay, V. Shutthanandan, D.R. Baer, S.A. Chambers*, Pacific Northwest National Laboratory

We report quantitative analysis of pulsed laser deposition (PLD) of $LaAlO_3/SrTiO_3$ heterostructures performed using X-ray photoelectron spectroscopy (XPS) and Rutherford backscattering spectrometry (RBS). Pulsed laser deposition (PLD) has been the method of choice for the growth of LAO/STO heterostructures in many laboratories. PLD practitioners generally assume that the stoichiometry of the target is preserved in the process of vaporizing and condensing the target material onto the substrate. However, researchers do not usually conduct detailed materials characterization measurements that would ensure that this assumption is valid. We recently initiated a study of the spatial distribution of condensed La and Al on 2” diameter Si substrates held at ambient temperature during PLD of a LAO target. The substrates were fixed in position relative to the laser plume and did not rotate during growth. We found that there is considerable spatial variation in composition of La and Al deposited on the Si from a single crystal LAO target, even at laser fluences well above the ablation threshold. The on-axis geometry, in which the axis of the laser plume intersects a portion of the substrate, clearly leads to a significant enrichment of La and an Al deficiency. Although the variations are apparent in both XPS and RBS, we have further quantified the composition in XPS by comparison with standards and sensitivity factors specifically determined for our instrument. A La to Al ratio of 1:1 is achieved only over a narrow range of off-axis plume angles. XPS and RBS determination of the composition as a function of position on the substrate will be reported. We present a comparison of XPS LAO quantifications with and without overlayer correction from surface adventitious hydrocarbon contamination using the La 4d line with a relatively high kinetic (KE) energy of 1,383 eV with a lower KE La 3d$_{5/2}$ line at 651 eV.

AS-TuP24 Complete Analysis of Materials using Complementary Techniques*, **V.S. Smentkowski**, D. Wark, L. Le Tarte, H. Piao, J.C. Chera, S.G. Ostrowski, A. Suzuki*, General Electric Global Research

A combination of complimentary analysis techniques has been used to characterize a diffusion couple sample. We will demonstrate that the results, when taken together, provide for a better understanding of the sample than the data from any one technique alone. The poster will summarize how diffusion couples are fabricated and highlight the benefits of each characterization technique. Electron Probe Micro Analysis (EPMA) provides for quantitative chemical analysis (spectrometry and imaging) of most elements (Z>4) at a concentration greater than about 0.1 % within a volume of 1-2 microns. EPMA also allows for imaging of both backscattered and secondary electrons. Auger Electron Spectroscopy (AES) has the smallest analytical spot, provides for quantitative analysis of all elements (except H and Li) present at concentrations of greater than about 0.5 atomic percent, and can perform high lateral resolution imaging. X-Ray Photoelectron Spectroscopy (XPS) provides for quantitative analysis of all elements (except H and Li) present at concentrations greater than about 0.5 atomic percent, is able to analyze insulating samples, and can provide information regarding the chemical state of the material. Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is able to detect all elements and high mass molecular fragment ions with high sensitivity, is able to analyze non-conductive samples, and the analyst does not need to select which species to analyze for prior to the measurement since a full mass spectrum is saved at every volume element. AES, XPS, and ToF-SIMS surface analysis instruments can operate in spectrometry modes (compositional analysis), imaging modes, as well as depth profiling modes (where one monitors the sample composition as a function of depth).

AS-TuP25 Field Emission from Two-Dimensional Electron Gas in Hetero-Junctions of InAlAs/InGaAs Multiple Quantum Wells*, **Y. Itakura**, M. Matsumoto, K. Fukutani, T. Okano*, The University of Tokyo, Japan

The two-dimensional electron gas (2DEG) in multiple quantum wells (MQWs) shows interesting electronic phenomena which are important for semiconductor device applications such as High Electron Mobility Transistor (HEMT). Due to a highly coherent feature and quantized energy levels, electron emission from 2DEG is expected to reveal spatially anisotropic patterns and a characteristic bias dependence. In this study, we applied a high electrostatic field to the surface of a semiconductor hetero-structure in aimed at exploring the physics of field emission from a 2DEG.

For the experiments, we developed a novel cleavage mechanism usable in the UHV environment to realize the high electrostatic field necessary for the tunneling through the potential barrier between the bulk and the vacuum allows for double cleavage along the <110> and <1-10> directions and thus creates a very sharp edge at the corner of a square-shaped wafer with a semiconductor hetero-structure. The cleavage under UHV is also indispensable to obtain clean surfaces free from oxidation. Observation of the apex of the cleaved edge by scanning electron microscopy confirmed that the curvature radius is sufficiently small to allow for field emission. The hetero-structure adopted for this study was an InAlAs/InGaAs modulation doped structure grown on oriented InP(001) substrate by molecular beam epitaxy (MBE). The composition of the hetero-structure was In$_{0.52}$Al$_{0.48}$As/In$_{0.53}$Ga$_{0.47}$As MQW with 2 periods of InGaAs wells, InAlAs spacers, and Si-doped InAlAs donor layers. The thickness of the spacer layer was 20 nm, and the sheet carrier density was approximately 1.0 x 10^{12} cm^{-2}.

In this presentation, we will report the spatial distribution of the field emitted electrons (field emission pattern) and the I-V characteristics of the field emission.

AS-TuP29 Characterization of Silver Nanoparticles Synthetized on Nylon Membranes Used as Nanoreactors*, **L. Huerta**,* Universidad Nacional Autónoma de México*, V. Sánchez-Mendieta, R.A. Morales-Luckie, S. Reyes-Vega,* Universidad Autónoma del Estado de México*, M. Flores,* CUCEI, Universidad de Guadalajara, México*, J. Arenas Alatorre*, Universidad Nacional Autónoma de México

We used X-ray photoelectron spectroscopy (XPS) method for the characterization of surface composition of core and shell silver nanoparticles. The samples were prepared in thin nylon membranes, by means of an easy method of impregnation and reduction of metal ions, using a NaBH$_4$ aqueous solution, at ambient condition. Particles of less than 10 nm were obtained using the nylon fibres as nanoreactors.

The mesoporous nylon fibres, as observed by scanning electron microscopy (SEM), along to the oxygen and nitrogen density from amide moieties in nylon, provide effective sites for *in situ* reduction of silver ions, and for the formation and stabilization of Ag nanoparticles, consistent with the XPS results, showing of the N *1s* core level a chemical shift with increasing concentration of metal particles of Ag. Transmission electron microscopy (TEM) analysis showed that silver nanoparticles were homogenously dispersed in the nylon templates.

Photoelectron spectroscopy analyses confirmed the composition of the clusters to be metallic status of Ag nanoparticles.

AS-TuP32 Transport Properties of Doped SiGeSn Alloys*, **V. D'Costa**, Y. Fang, J. Menendez, J. Kouvetakis*, Arizona State University

A tunable direct absorption edge has already been demonstrated in lattice-matched SiGeSn alloys grown on Ge-buffered Si [1]. These alloys represent the first practical group-IV ternary making it possible to decouple electronic structure and lattice parameter. This opens up new possibilities in IR optoelectronics and photovoltaics [2,3]. The d oping of ternary alloys is a basic requirement for device applications. N-type doping is achieved using (SiH$_3$)$_3$P whereas diborane is used to obtain p-type SiGeSn. In this paper, we focus on the transport properties of SiGeSn alloys. The dielectric function of heavily-doped alloys has been measured using infrared spectroscopic ellipsometry. The infrared response of the ternary alloys is Ge-like and is dominated by the free carrier contribution. In addition, the dielectric function of p-type alloys shows features due to optical transitions between split-off (SO), light-hole (LH), and heavy-hole (HH) bands. Our studies confirm that doping can be achieved in the ternary alloys. The resistivities and mobilities of the alloys are comparable to those found in Ge samples with similar doping concentrations. We are currently studying the transport properties of lattice-matched alloys as a function of Si and Sn concentration.

1. V.R. D’Costa et al, Phys. Rev. Lett 102**,** 107403 (2009)

2. R. A. Soref et al, Journal of Materials Research 22, 3281 (2007)

3. F. Dimroth and S. Kurtz, MRS Bull. 32, 230 (2007).

AS-TuP33 Topographical Study of TiN "Ion-CCD" Detector Surface: How damaging are sub-fA Ion Beams of 1-keV Energy?*, **O. Hadjar**, G. Kibelka*, O.I. Analytical

The development of ion-detector arrays with high spatial resolution enabled the miniaturization of double-focusing sector-field mass spectrometers (MS). A modified imager based on a charge-coupled device (CCD) provides the spatial resolution, ruggedness, and analytical sensitivity necessary to build a transportable mass spectrometer. The transportable (~ 40 lb) mass spectrometer, which was introduced by OI Analytical at the 2009 Pittsburg Conference[1], is based on a double-focusing sector-field MS of Mattauch-Herzog geometry and an ion-CCD. The MS separates ions of different m/z spatially and focuses all ion beams onto a confocal plane of 2” width. The ion-CCD detects simultaneously all separated ion beams. The focal point of an ion beam is about 1500 x 300 mm^2, covering roughly 10 pixels. The ion-CCD consists of 2126 active pixels with a pitch of 24 µm. *Fig.1* is a contact mode Atomic-Force-Microscope image showing the width (21 µm) of the pixel and the insulation gap between two adjacent pixels (3 µm). The ion-CCD as described earlier[2] has an upper layer of TiN, 100- nm thick. It is this layer that takes the full impact of the up to 1- keV ions at an incidence angle of 45^{o}. In this work we will investigate the effect of the energetic ions on the ion-CCD and probe the extent of the surface damage, if any, as function of the ion flux and the overall ion-CCD exposure time. The ion-CCD is generally exposed to ion currents in the sub-fA regime and ion beam densities of up to about 109-1011 ions/cm^2 per second. We will characterize an ion-CCD chip after operating for roughly one year and compare pixels with no ion impact history to those exposed to ion beams consisting of N$_2^+$, O$_2^+$, Ar$^+$ and Xe$^+$. In our system, the impact energy of the analyzed compounds falls right on the efficient sputtering regimes, especially for ions with masses close to N and Ti where momentum transfer is optimum[3].

(1) "Compact GC/MS based on the Ion-Camera mass spectrometer", Gottfried Kibelka, Omar Hadjar, Scott Kassan, Scott Shill, Chad Cameron. Pittsburgh Conference, Chicago. 2009.

(2) "CCD for Ion Detection" Omar Hadjar, Gottfried Kibelka, AVS International Symposium & Exhibition, Boston 2008.

(3) J. Vac. Sci. Technol. A, Volume 19, Issue 3, pp. 1004-1007 (May 2001).

Biomaterial Interfaces
Room: Hall 3 - Session BI-TuP

Biomaterial Interfaces Poster Session I

BI-TuP2 Formation of Stable Microbubbles by Encapsulation in Silica, ***K. Staggs***, University of New Mexico, *G. Gupta*, Los Alamos National Laboratory, *M. Tartis*, New Mexico Tech, *G.P. Lopez*, University of New Mexico

A new technique for stabilization of supramolecular assemblies (termed soft petrification) has been applied to the stabilization of microbubbles. Commonly used as ultrasound contrast agents, most types of microbubbles are inherently unstable. Current procedures require many types of microbubbles to be filled with hydrophobic, high molecular weight gases such as octafluoropropane and perfluorobutane. Special equipment including syringe pumps and sealing devices are required, because most microbubbles must be formed under these types of gases. This requirement limits the conditions under which microbubbles can be studied. They cannot be studied on a bench top open to atmosphere. Once microbubbles have undergone soft petrification, they can be studied in a wide range of environments. In soft petrification of air filled lipid coated microbubbles, a vapor deposition technique encapsulates the microbubbles in a thin silica shell. After undergoing soft petrification, it was observed that microbubble stability under adverse conditions is significantly improved. These adverse conditions include pressures up to 120 psig and temperatures up to 80°C. Those values are double the values found for microbubbles without the silica shell. Other unique characteristics of these microbubbles include the ability to withstand temperatures well below freezing, without loss of size. Air filled microbubbles have a bench top life span of approximately four hours before encapsulation. Following encapsulation, it is observed that the same microbubbles have a bench top lifespan of up to several months. Several formulations were characterized and unprecedented air filled microbubble studies are facilitated by this technique.

BI-TuP3 Synthesis of Grafted PNIPAAm Surfaces Using ATRP in Presence of Air for Cell Adhesion Studies, ***P. Shivapooja***, *L.K. Ista, S. Mendez, G.P. Lopez*, University of New Mexico

Poly(N-isopropylacrylamide) (PNIPAAm) is a thermoresponsive polymer that exhibits a change in relative hydrophobicity above and below its lower critical solution temperature (LCST ~ 32^0C). This stimuli responsive polymer when grafted onto surface can act as a biofouling resistant coating as it has the property of formation and collapse of hydrogen bonding with water molecules below and above the LCST. Atom transfer radical polymerization (ATRP) has been proven to yield well-defined polymer but in rigorously deoxygenated environment, for example in a Schlenk line or glove box. Matyjaszewski *et al.* group developed activators regenerated by electron transfer (ARGET) that allow ATRP in presence of limited amount of air *[Langmuir 2007, 23, 4528-4531]*. We report grafted PNIPAAm brushes synthesized by this relatively simple method of ARGET ATRP which does not require an oxygen-free environment using a small amount of reducing agent together with a catalyst under homogeneous conditions. We evaluated the effect of the amount of reducing agent and reuse of monomer solution on the grafting thickness. The grafted PNIPAAm surfaces have been characterized by FTIR, XPS, contact angle measurements and ellipsometry. We anticipate using these grafted PNIPAAm surfaces for cell adhesion studies above and below the LCST.

BI-TuP4 Undercovering the Extracellular Matrix with Thermoresponsive Microgels, ***J.A. Reed***, University of New Mexico, *R.K. Shah, T. Angelini, D.A. Weitz,* Harvard University, *H.E. Canavan*, University of New Mexico

The extracellular matrix, or ECM, remains a hidden biological interface between a cell and a substrate. One method for examining proteins, such as those in the ECM, is flow cytometry (FC), which is a fast, high throughput method of quantification. Since FC is a solution technique, it is necessary to dissociate the cells from the surface. Traditional cell harvesting methods, such as enzymatic digestion and physical scraping, damage the ECM proteins as well as the cell morphology. Recently it has been shown that a thermoresponsive polymer, poly(N-isopropyl acrylamide) or pNIPAM, can be used to harvest a sheet of cells without damaging the integrity of the ECM. Above its lower critical solution temperature (LCST), this 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 more hydrophilic and swelling. Furthermore, when the temperature of the cell culture is dropped below the LCST of the polymer, the cells will detach as an intact cell sheet. These intact cell sheets, however, are not ideal for investigation in a flow cytometer, which requires individual cells for quantification. In this work, we developed a novel method for single cell detachment using pNIPAM microgels on the order of 20-200 micrometers. After fabrication, these gels were examined to ensure pNIPAM's characteristic thermoresponse was maintained, followed by cell culture on the gels. From these results, we conclude that these microgels have the capability of giving us access to this buried biological

BI-TuP5 Facile C-terminal Attachment of Proteins on Surfaces by Hydrazine-Intein Chemical Reactions, ***P. Yang***, *S. Marinakos, A. Chilkoti*, Duke University

Protein immobilization on surfaces is important in many areas of research, including their biophysical characterization, affinity chromatography, and heterogeneous immunoassays. We describe a new site-specific C-terminal immobilization of proteins on surfaces to control the orientation and attachment point of the protein. Our strategy was to exploit intein chemistry and the related hydrazine attack reaction. To provide-proof-of principle of this approach, a tripartite thioredoxin-intein-elastin-like polypeptide (ELP) fusion was synthesized in E. coli from a plasmid-borne gene. In this fusion protein, the C-terminus of the target protein thioredoxin was fused with the N-terminus of an intein, a self-splicing protein domain. An ELP was fused to the C-terminus of the intein to facilitate purification of the fusion protein because ELP fusions allow simple purification of proteins from cell lysate by isothermal, salt-triggered phase transition of the ELP. Incorporation of the intein at the C-terminus of the target protein provided an unnatural peptide bond between the target protein and the intein, which is selectively reactive towards nucleophiles such as hydrazine. In order to immobilize the target protein –thioredoxin– a hydrazine-functionalized surface on a protein-resistant background was fabricated by modifying a gold-coated glass substrate with a mixed self-assembled monolayer consisting of a hydrazine-terminated hexa(ethylene glycol) thiol and a tri(ethylene glycol)thiol. We demonstrate that the hydrazine groups on the surface were able to directly attack the unnatural peptide bond between the target protein and the intein, liberating the thioredoxin from the tripartite fusion and covalently attaching it to the surface. As a result, the target protein was site-specifically immobilized on the planar substrates with uniform orientation. This technique provides many advantages over other site-specific immobilization methods, including faster reaction kinetics, higher surface density, and the ability to easily purify the protein prior to immobilization though a simple, one-step non-chromatographic process that exploits the phase transition of the ELP.

BI-TuP6 Fabrication and Characterization of Non-toxic and Non-Biofouling Plasma-Polymerized Polyethylene Glycol Thin Films, ***C. Choi***, *K.S. Kim, D. Jung,* Sungkyunkwan University, Rep. of Korea, *D.W. Moon, T.G. Lee*, KRISS, Rep. of Korea

Polyethylene glycol (PEG) is a key molecule in the fabrication of non-biofouling surface for various biological applications such as biochips and tissue engineering. In particular, plasma-polymerized PEG (PP-PEG) thin films have many practical uses due to their strong adhesion onto any solid substrates. In this work, we fabricate PP-PEG thin films by using the capacitively coupled plasma chemical vapor deposition (CCP-CVD) method and non-toxic PEG200 molecules as a precursor. The surfaces of the PP-PEG thin films were characterized by using contact angle measurement, X-ray photoelectron spectroscopy (XPS), atomic force microscopy (AFM), Fourier transform infrared (FT-IR) spectroscopy and time-of-flight secondary ion mass spectrometry (TOF-SIMS). Our results show that PP-PEG thin film surfaces deposited at low plasma power were very similar in chemical composition to the PEG polymer surfaces. In addition, these PP-PEG surfaces showed excellent non-biofouling property and biocompatibility during *in vitro* and *in vivo* tests. These results indicate that our PP-PEG thin films would be useful for practical biological applications.

BI-TuP7 Optimization of Elastin-Like Polypeptide Fusions for the Purification of Membrane Proteins by Inverse Transition Cycling, ***T. Thapa***, *S. Simons, E. Chi,* University of New Mexico, *A. Chilkoti,* Duke University, *G.P. Lopez*, University of New Mexico

Low column efficiency is a common problem associated with the affinity purification of surfactant solubilized membrane proteins synthesized in recombinant and cell free expression systems. Elastin-like polypeptide (ELP) tags, which have been designed to allow non-chromatographic purification of soluble proteins, offer a potential means to enable facile large-scale purification of detergent solubilized recombinant membrane proteins. However, the phase transition temperature (T_t) of ELPs is sensitive to the addition of cosolutes and many detergents increase the T_t of ELPs to temperatures greater than the thermal denaturation temperature of many proteins that are fused to the ELP, hence prohibiting their use for protein purification. To identify detergents that would satisfy the dual and potentially conflicting requirements of stabilizing membrane proteins fused to an ELP, we screened different detergents with respect to their effect on the T_t of ELP[$V_5A_2G_3$-180]. We found that dodecyl maltoside (DDM), a detergent that is commonly used to solubilize recombinantly expressed membrane proteins, did not significantly alter the phase transition characteristics of ELPs or their structure as probed by a temperature-programmed turbidity assay and circular dichroism spectroscopy. Our results clearly indicate that DDM does not affect the inverse transition cycling of ELPs and therefore may be useful to purify membrane proteins which are otherwise difficult to extract and purify by affinity chromatography.

BI-TuP8 Self-assembly of Proteins on Well-defined Sapphire Surfaces, ***T. Isono***, *K. Yamazaki, T. Ogino*, Yokohama National University, Japan

Non-specific adsorption is a very serious issue when biomolecules are immobilized on solid surfaces. Non-specific adsorption should be suppressed especially in application of solid surfaces to biosensors or implant devices. We have tried to control protein adsorption on step-controlled sapphire surfaces. Because sapphire surface is chemically stable in liquid as well as in air, it is a suitable material for bioapplication. To control interactions between the sapphire surfaces and protein molecules, we designed surface atomic structures. In this study, we report on self-assembly of several kinds of protein molecules by using well-defined sapphire surfaces. Single crystalline sapphire (0001) surfaces were used for protein adsorption. By a high temperature annealing, the sapphire surfaces are covered with bunched steps accompanied with crossing steps when the miscut direction slightly tilts from the stable direction of atomic steps. These surfaces were cleaned by a mixture of sulfuric acid and hydrogen peroxide. We call this surface oxidized surface. Two domains, which exhibit different hydrophilicity and charge density from each other, coexist on this surface. Center regions of the terraces (domain A) are relatively hydrophobic and weakly charged, and the others (domain B) hydrophilic and negatively charged. To control the surface chemical properties, the oxidized surfaces were slightly etched by phosphoric acid. We call this surface etched surface. Protein molecules were physically adsorbed on the oxidized and the etched surfaces in a buffer solution. Protein adsorption patterns were observed by atomic force microscopy in the same buffer solution. When the oxidized surfaces were immersed in a solution of ferritin molecules whose surfaces exhibit a negative charge, ferritin molecules were selectively adsorbed on the domain A by the electrical repulsion between the domain B and the molecules. On the other hand, avidin molecules whose surfaces exhibit a positive charge were selectively adsorbed on the domain B by the attractive interaction. These protein molecules were adsorbed on the sapphire surfaces depending on the surface charges. However, small amount of avidin molecules were adsorbed on the hydrophobic domain A. Generally, it is easier for protein molecules to be adsorbed on hydrophobic surfaces than hydrophilic ones. To make the domain A hydrophilic, the oxidized surfaces were etched using phosphoric acid. When the etched surfaces were immersed in a solution of avidin molecules, avidin molecules were selectively adsorbed without non-specific adsorption on the domain A.

BI-TuP10 Lubricin Prevents Degenerative Changes in Articular Cartilage Structure and Morphology, ***J. Coles***, Duke University, *C. Cha*, Brown University, *M. Warman*, Boston Children's Hospital, *G. Jay*, Brown University, *F. Guilak, S. Zauscher*, Duke University

Lubricin is a mucin-like glycoprotein which contributes to boundary lubrication in joints and is also thought to have a role in protecting cartilage surfaces. Direct studies of joint protection by lubricin have been difficult but a lubricin null mouse has been developed recently, providing completely lubricin-free cartilage for study. We have shown that atomic force microscopy can be used for measurements of interfacial friction in the boundary lubrication regime and use this technique to measure friction directly on cartilage not expressing lubricin. We further use atomic force microscopy and histology to characterize stiffness and surface and subsurface morphology of these joints. While friction measured directly on lubricin null cartilage was only slightly lower than on wild type cartilage, surface structure and mechanical integrity were altered significantly. Lubricin null cartilage surfaces were significantly rougher, stiffness did not develop normally, and glycosaminoglycan (a core structural component of cartilage) concentration near cells was lost as joints developed. While reduction of friction is likely an important factor in lubricin's role in protecting cartilage, our measurements on lubricin null cartilage suggest that lubricin may additionally protect cartilage through other mechanisms.

BI-TuP11 Plasma Polymerization Induced Structural Modification of PCL, ***A.M. Sandstrom***, *L. Grøndahl, J.J. Cooper-White*, University of Queensland, Australia

Cellular response to tissue culture scaffolds is thought to be directed by chemical and topographical cues from surfaces which bind biological motifs recognized by cell receptors. Plasma polymerization (PP) is frequently used to functionalize surfaces for improved biocompatibility. It has been reported that the type and distribution of functional groups created on a surface is dependent on plasma parameters. However, in addition to changing chemistry, modification of plasma parameters is also likely to introduce topographical variation to the sample. The aim of this work was to elucidate the combined effects of plasma power and treatment time on the surface chemistry and topographical features of the substrate.

Scaffolds [5% poly(ε-caprolactone) (PCL)/1,4-dioxane] were prepared using thermally induced phase separation. Samples were plasma polymerized in a custom-built radio frequency reactor using heptylamine (HA) at 20W and 50W for 30s and 60s. Additional substrates were prepared by spincoating PCL on Si wafers. For each of the four treatment conditions, surface homogeneity was confirmed across the wafers and scaffold sections via XPS. Surface topography was investigated on wafers by AFM, and scaffolds were examined using SEM.

Disappearance of the PCL carboxyl (C=O) peak following PP for all treatment conditions suggests complete coverage (>10nm) of the top surface of all substrates by PPHA. The N/C ratio was slightly higher on the Si wafer than the scaffold. Treatment was homogenous across individual samples. Slight chemical functionality shifts were found between samples, which may reflect intrinsic plasma differences or post-PP oxidative variation.

Polymer aggregates formed on Si following PPHA treatment at 20W, but were diminished at 50W. Topographical changes were more pronounced on PPHA PCL-coated Si. Although spherulite size variation was minimal between untreated semi-crystalline PCL and PPHA PCL on Si for most treatments, complete recrystallization of the base polymer was observed at 50W 60s. Change in surface roughness was evidenced by disappearance of well-defined fibrous domains as treatment power and time increase for all samples, except at 50W 60s when distinct spherulites re-emerged.

Highly reactive HA recombination led to aggregate size reduction on Si, whereas PPHA on PCL appeared to affect structural organization of the substrate. Scaffold morphology also changed following PPHA, as more energetically favored fibrous extensions in the porous region of the surface were observed by SEM. These results may be used in conjunction with cellular studies to tune PPHA reactions on scaffolds as required for support of various cell types.

BI-TuP12 Molecular Dynamics Simulation of Interactions between Structured Peptides and Functionalized Solid Surfaces, ***G. Collier***, *R.A. Latour, S.J. Stuart*, Clemson University

The chemical and physical interactions between proteins and biomaterial surfaces govern the biocompatibility of those materials when introduced into a living system. Therefore, the possibility of controlling biocompatibility on a molecular level through the strategic design of biomaterials begins with the study of these interactions at the atomic level. Without an accurate molecular description of the way that proteins interact with biomaterials, biomaterial design is primarily relegated to a trial-and-error approach. To address this issue, we have begun to evaluate the applicability of existing all-atom molecular simulation methods and force fields to the unique situation of simulating the interaction of structured peptides with solid biomaterial surfaces.

Today's most advanced molecular modeling tools do not include parameterization options for molecular systems interacting with solid biomaterial surfaces, so we have undertaken a variety of pilot studies to guide the development of our methods for use in more complex simulations. These pilot studies include nanosecond-scale simulations of structured peptides interacting with charged and uncharged self-assembled monolayer (SAM) surfaces, ion distributions over a charged SAM surface, peptide-peptide interaction studies, peptide stability studies, analysis of environmental changes resulting from peptide conformation changes, and analysis of the role of water molecules in the peptide-surface adsorption process. The adsorption and stability studies are being conducted using multiple molecular modeling force fields, enabling a comparison of their performance and usefulness in the simulation of these unique systems. The majority of this work has been conducted using replica-exchange molecular dynamics (REMD) techniques in order to optimize conformational sampling, resulting in the most efficient path toward structural data that can be compared with experimental results.

The results from these studies are enabling us to assess the suitability of currently available molecular simulation methods and force fields and are providing us with a better understanding of peptide-surface interactions at the atomic level.

BI-TuP13 ToF-SIMS Study of Fibronectin Orientation on Self-Assembled Monolayers, ***L. Árnadóttir***, *J. Brison, L.J. Gamble*, University of Washington

Protein adsorption and orientation plays a critical role in many biomedical applications. Fibronectin (FN) is an extra cellular matrix protein that is involved in many cell processes such as adhesion, migration and growth. The orientation and conformation of FN adsorbed onto surfaces can therefore have a critical effect on cell-surface interactions. In this study the adsorbed orientation and conformation of the 7-10 fragment of FN ($FNIII_{7-10}$) was studied on four different model surfaces (self-assembled monolayers (SAM) of C_{11} alkanethiols on Au, $-CH_3$, $-NH_2$, -COOH and -OH terminated SAM). The $FNIII_{7-10}$ fragment incorporates both the Arg-Gly-Asp (RGD) FN receptor binding motif and the PHSRN synergy site which participate in the RGD binding. The effect of different surface chemistries on binding and adsorption configuration was investigated using X-ray photoelectron spectroscopy (XPS) and time of flight secondary ion mass spectrometry (ToF-SIMS). XPS showed significantly higher protein coverage on the hydrophobic $-CH_3$ terminated surface than the hydrophilic and negatively charged –COOH terminated surface. Both XPS data and SIMS peak intensities for certain amino acid were used to verify the adsorption process and monolayer coverage. Full coverage was determined by a plateau in SIMS peak intensities with increasing protein exposure. A principal component analysis (PCA) of the ToF-SIMS data on surfaces with similar sub-monolayer protein coverage was then used to determine changes in the spectra that differed when the fragment was adsorbed on various surfaces. These results are related to different orientation or conformations of the fragment on the different surfaces.

BI-TuP14 Wear-Rate Behavior of Hydroxyapatite-Coated Titanium, ***A.F. Jankowski***, Texas Tech University

Calcium phosphate-based ceramics are used in medicine and dentistry due to excellent biocompatibility with human tissues. The formation of hydroxyapatite coatings with a porosity gradient on the surface of metal implants can provide a surface suitable for the in growth of connective tissue. A need exists to both protect the metal substrate against corrosion and provide sufficient mechanical adhesion. Hydroxyapatite coatings have been produced by the reactive, radio-frequency sputtering of stoichiometric $Ca_{10}(PO_4)_6(OH)_2$ targets using planar magnetrons onto titanium-coated silicon substrates. A fully dense and thin initial-coating layer appears to avoid cracking, improves substrate adhesion, and provides corrosion protection (J. Mater. Res. 16, 2001, 3238). The effect of varying the wear rate is now evaluated on the mechanical behavior of sputter deposited hydroxyapatite coatings.

BI-TuP15 Asymmetric Hybridization Behavior Exhibited by DNA Probes Containing Surface-Attachment Ligands and Self-Complementary Sequences, *S.M. Schreiner, D.F. Shudy,* University of Wisconsin, ***D.Y. Petrovykh***, Naval Research Laboratory and University of Maryland, College Park, *A. Opdahl*, University of Wisconsin

We demonstrate the impact that intra-molecular and nucleotide-gold interactions have on conformation of surface-immobilized DNA probes and their hybridization behavior. We take advantage of a method based on the intrinsic affinity of adenine nucleotides for gold (Opdahl et al., PNAS, **104**, 9–14, 2007) to immobilize block-oligonucleotides having sequences that follow a $d(A_k\text{-}T_m\text{-}N_n)$ pattern: a block of *k* adenines $[d(A_k)]$, followed by a block of *m* thymines $[d(T_m)]$, and a block of *n* (arbitrary) nucleotides $[d(N_n)]$. Such block-oligos assemble on gold via the d(A) blocks, which allow a high degree of control over DNA surface coverage and conformation. We characterize immobilization and hybridization of these DNA probes using x-ray photoelectron spectroscopy (XPS) and surface plasmon resonance (SPR) imaging, specifically to compare two 15-nucleotide N_n sequences: 15 thymines (T15) and a realistic arbitrary sequence (P15). For A15-T5-P15 probes, the hybridization efficiency at the P15 end is enhanced 2-fold compared to that at the A15 end. For A15-T20, which forms a hairpin in solution, we observe a larger asymmetry of hybridization efficiencies when immobilized on gold: while the T15 end is highly accessible for hybridization, the A15 end has virtually no hybridization activity. A thiolated version of the same probe (A15-T20-SH), in contrast, exhibits little asymmetry and overall low hybridization efficiency with either A15 or T15, consistent with an immobilized structure of a stable hairpin. Additional experiments, whereby a displacement thiol is added to reduce DNA-gold interactions, are used to support our inferences about the role played by intra-molecular and surface interactions in immobilization and hybridization of DNA probes.

Electronic Materials and Processing
Room: Hall 3 - Session EM-TuP

Electronic Materials and Processing Poster Session

EM-TuP1 Direct Growth of Hexagonal InN Films on 6H-SiC by RF-MOMBE, ***W.-C. Chen***, *C.N. Hsiao,* National Applied Research Laboratories, Taiwan, *D.P. Tsai*, National Applied Research Laboratories and National Taiwan University

Wurtzute InN films were prepared on 6H-SiC substrate by self-designed plasma-assisted metal-organic molecule beam epitaxy system without buffer layer. In our report, we discussed the effects of substrate temperature on structural and optical properties of InN films. The crystalline and microstructure of the thin film was further characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), respectively. Electrical and optical properties were evaluated by Hall and photoluminescence (PL) measurements. XRD results indicated that InN films were polycrystalline and preferential grown along c-axis orientation. Two-dimensional growth mode was clearly shown from SEM images. However, cracks due to the lattice and mainly large thermal expansion coefficient mismatch were observed as well. Cross-sectional TEM images revealed that the InN films were grown continuously from the 6H-SiC substrate, and c-axis lattice constant was about 0.57 nm. Room-temperature PL spectra showed the emission peak is located at ~ 0.83 eV and sheet carrier concentrations is 7.9×10^{15} cm^{-2}. It was found that the optoelectronic properties and crystalline quality can be improved significantly by optimizing growth temperatures.

EM-TuP2 Evolution of the Electrical Conductivity of Amorphous Carbon Nitride Films in Terms of Disorder Parameters and Density of States, *F. Alibart, O. Durand-Drouhin, A. Zeinert, M. Benlahsen,* ***M. Lejeune***, LPMC - UPJV, France

In this study, we discuss the correlations between electrical and optical properties of highly sp^2 amorphous carbon nitride for the development of electronic devices applications. The amorphous carbon thin films have been deposited using reactive plasma ($Ar+N_2$) radio frequency magnetron sputtering. The partial pressure of nitrogen has been used to vary the optoelectronics properties of the films.

The optical gap has been investigated using UV-visible-NIR spectroscopy and linked to the disorder parameter W^{-1}. The electrical conductivity has been studied in the temperature range of -170°C to 300°C and has revealed the presence of two conductivity modes. These results have been interpreted as a function of the density of states (DOS) evolution. The microstructural evolutions of the films with nitrogen incorporation have been investigated by Raman spectroscopy and IR absorption spectroscopy.

The disorder parameter W^{-1} has shown a linear dependence with the optical gap in this range of materials (highly sp^2 carbon films) and has been interpreted as a measure of the overall disorder (structural and topological). At low nitrogen partial pressure, nitrogen incorporation promotes the graphitization and the clustering of the sp^2 phase. The preferential contribution of disorder has been identified as an increase of topological disorder (cluster size dispersion). The increase of electrical conductivity in this stage has been correlated to the increase of disorder and has revealed an increase of the sp^2 connectivity consistent with an increase of the cluster size.

The decrease of conductivity for the higher nitrogen content has been interpreted in a specific model for highly sp^2 materials (adaptation of Robertson's two phase model). The proportion of CN triple bonds has been identified as a major effect on the material connectivity affecting the optoelectronic properties of the films.

EM-TuP3 Characterization of $Zn_{1-x}Mn_xO$ / ZnO Hollow Nanosphere Structures, ***D.R. Liu***, Instrument Technology Research Center, Taiwan, *W.H. Cho, C.Y. Su,* National Applied Research Laboratories, Taiwan, *D.P. Tsai*, National Taiwan University

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, ZnO layer was conformally deposited on the surface of polystyrene (PS) nanoshpere by atomic layer deposition (ALD). After removal of PS nanosphere by heating, ZnO hollow nanospheres were formed. Then the

Zn$_{1-x}$Mn$_x$O (x=0~0.1) coatings were grown on ZnO hollow nanospheres by Nd:YAG pulsed laser deposition(PLD). According to the results of high-resolution x-ray diffraction, the Zn$_{1-x}$Mn$_x$O / ZnO hollow nanospheres are polycrystalline with a preferential growth direction of (002). Atomic force microscopy (AFM) and magnetic force microscopy (MFM) images show that the magnetic properties of Mn doped ZnO hollow nanospheres strongly depend on the Mn composition fraction and the size of nanospheres. Photoluminescence spectra demonstrate ultraviolet emission peaks which have shift with the increase of Mn ion concentration. The temperature-dependent magnetization (M-T) curves of the Zn$_{1-x}$Mn$_x$O hollow nanospheres were measured by a superconducting quantum interference device (SQUID) magnetometer and also depend on the Mn composition fraction and the size of nanospheres.

EM-TuP5 Lifetime and Defect Characterization of Engineered Germanium-on-Silicon Wafers for III-V Photovoltaics, ***J. Sheng***, *D. Leonhardt,* University of New Mexico*, J.G. Cederberg, M.S. Carroll,* Sandia National Laboratories*, S.M. Han*, University of New Mexico

Demand for low-cost, light-weight, mechanically strong, high-efficiency multijunction solar cells has motivated the development and use of high-quality Ge-on-Si (GoS) heterostructures to integrate III-V films. However, such integration poses many engineering challenges, ranging from lattice mismatch, to thermal expansion coefficient mismatch, to non-planar morphological evolution. To eliminate antiphase domain (APD) boundaries in GaAs grown on GoS, in particular, the Ge surface on GoS substrates must maintain the crystallographic off-cut of the underlying Si. Here, we report a slurry-free chemical-mechanical polish step used to planarize the GoS surface. The root mean square (RMS) roughness of the resulting Ge surface is less than 1 nm. We have also characterized polished GoS substrates for their electrical properties. Due to nanoscale heterojunction engineering involving a SiO$_2$ template, the experimentally measured recombination velocity (SRV) at the Ge-Si interface approaches 9 x 10^3 cm/s. Capacitance-voltage (C-V) measurements are also used to determine the density of electrically active defects in the Ge layer of the GoS heterostructure. The *p*-type defect density is approximately 2 x 10^{16} cm^{-3}. Currently, more steps are taken to reduce the density of active defects.

EM-TuP6 Imaging Characterization Techniques Applied to Cu(In, Ga)Se$_2$ Solar Cells, ***S. Johnston***, National Renewable Energy Laboratory*, N. Call,* Colorado School of Mines*, R. Sundaramoorthy, I. Repins*, National Renewable Energy Laboratory

Imaging techniques developed over the past few years have the potential for quick and useful solar cell characterization. While initially applied to silicon, imaging techniques such as photoluminescence imaging, electroluminescence imaging, and lock-in thermography can also be successfully incorporated into Cu(In,Ga)Se$_2$ solar cell development and process feedback. These techniques are capable of collecting images that provide values of minority-carrier lifetime, diffusion length, series resistance, and shunting. While point measurements such as transient decay lifetimes yield quantitative results that are valuable to research and development, imaging data can often be collected in seconds or less with better spatial resolution and be correlated to important solar cell parameters.

EM-TuP7 High Rate Deposition of TiO$_2$ Films by Reactive Sputtering for Dye Sensitized Solar Cells*, Y. Sato, T. Hashimoto, A. Miyamura,* ***Y. Shigesato***, Aoyama Gakuin University, Japan

Dye-sensitized solar cells have attracted attentions as next generation solar cells which have possibility to perform high efficiency with low cost. In recent years, various applications of the cells, such as colorful or flexible solar cells fabricated on polymer substrates, have been suggested. In conventional processes to form the TiO$_2$ photoelectrodes in the cell, the substrates should be annealed at higher temperature than 500 °C, which make it difficult to deposit TiO$_2$ films on polymer substrates. Sputter depositions should have advantages in fabricating the window-size uniform coatings of anatase TiO$_2$ at low temperature. In this study, dye-sensitized solar cells with TiO$_2$ photoelectrodes deposited by reactive magnetron sputtering on flexible substrates were fabricated and characteristics of the cells were investigated. A dual magnetron sputtering (DMS) system was used for the sputter deposition of TiO$_2$ [1-3]. This system consists of two magnetron cathodes with Ti metal targets, a dc power source with a 50 kHz pulse unit and plasma control unit (PCU) with a feedback system of plasma emission intensity (Fraunhofer Institut fur Elektronenstrahl-und Plasmatechnik, FEP). In the PCU, the plasma emission intensity of the Ti line at 500 nm was transformed into photovoltage (OEI) in order to control O$_2$ flow ratio. TiO$_2$ films were deposited on ITO/PET films and FTO glass substrates. Unipolar pulse or pulse packet modes were used for the sputter depositions. In order to control O$_2$ flow ratio in "transition" and "oxide" regions, oxidation of the target surface was precisely controlled using the feedback system. Sputtering power of each target was kept at 5 kW. Film thickness of TiO$_2$ was 3-10 μm. A sandwiched photovoltaic device was fabricated with N3-sensitized TiO$_2$ photoelectrode and Pt-coated glass as a counter electrode. The deposition rates of both the pulse modes were about 7 nm/min in the "oxide region" and about 40 nm/min in the "transition region". The maximum value of conversion efficiency in this study was 3.7 % which was obtained in the cell with TiO$_2$ deposited with unipolar pulse mode in the oxide mode on FTO glass substrate. On the other hand, the cell with TiO$_2$ deposited in the pulse packet mode on ITO PET-films performed 1.25 %. Furthermore, we also recognized that TiO$_2$ with high photocatalytic decomposition activity showed high conversion efficiency where TiO$_2$ with poor photocatalytic activity showed poor conversion efficiency.

[1] S. Ohno, Y. Shigesato, et al., Thin Solid Films 445 (2003) 207.

[2] S. Ohno, Y. Shigesato, et al., Jpn. J. Appl. Phys. 43 (2004) 8234.

[3] S. Ohno, Y. Shigesato, et al., Thin Solid Films 496 (2006) 126.

EM-TuP8 Life-time Improvement of CdTe/CdS Solar Cells by Application of TiN Diffusion Barrier to Cu$_2$Te Back Contacts*,* ***C. Lim****, J. Park, S. Ryu,* Chosun University, Korea*, N. Kim,* Chonnam National University, Korea*, W Lee*, Chosun University, Korea

CdTe is one of the most convincing materials for thin-film solar cells shaped as the CdTe/CdS heterojunction structure. The formation of back contact is the most important and immediate problem to be solved with the low-resistance and excellent stability because the formation of an ideal ohmic contact to CdTe is very difficult with the most metals. Copper (Cu) compounds or copper-doped materials were generally employed for the back contact including ZnTe:Cu, Cu$_x$Te, Cu$_x$S, and Cu-doped graphite due to its high electrical conductivity, and similar electron affinity to CdTe. However, copper is easily and rapidly diffused to CdTe material; the life-time of CdTe/CdS solar cells is remarkably reduced because the diffused impurity of copper play roles of recombination center and shunt pathway. Therefore, the investigations for an improvement of life-time were widely performed on the formation of the alternative materials without copper or the heat-treatment of copper-containing materials. In this study, a diffusion barrier layer of TiN for an anti-diffusion of copper was employed with the Cu$_2$Te back contacts. TiN is well known as the diffusion barrier because of its good thermal/chemical stability, and low contact-resistance. The relation between the thickness of TiN layer and the diffusion of copper was analyzed by AES depth profile. The energy conversion efficiency and life-time at the optimized thickness was compared and analyzed to the specimen without the passivation layer. The improved life-time of CdTe/CdS solar cells with the good energy conversion efficiency was successfully obtained by the application of the optimized thickness of TiN diffusion barrier.

EM-TuP9 Intermediate Band Optical Transitions in ZnTe:O for Photovoltaics*, W. Wang, S.C. Lin,* ***J.D. Phillips****,* The University of Michigan*, W.K. Metzger*, National Renewable Energy Laboratory

The introduction of radiative electronic states within the bandgap of a semiconductor provide a mechanism for enhanced absorption of solar radiation and corresponding increase in short circuit current, while maintaining a large open circuit voltage. Approaches to introduce an intermediate band include the incorporation of quantum dots and doping of isoelectronic impurities. One promising material system is ZnTe (E_G=2.3eV), where the incorporation of oxygen provides a highly radiative state 0.4eV below the conduction band. In this work, the optical properties and photovoltaic response of ZnTe:O grown by molecular beam epitaxy on GaAs substrates will be presented. Photoluminescence measurements confirm a strong radiative transition for oxygen doping. Time-resolved photoluminescence measurements indicate a fast decay process from the conduction band, and a slow radiative decay from the oxygen states. Diodes consisting of ZnTe:O absorbers confirm that the response wavelength is extended to wavelengths beyond 900nm. Measurements consisting of two-photon excitation at wavelengths below the bandedge (650nm and 1550nm) further confirm transitions via intermediate band states. A device model for ZnTe:O intermediate band solar cells will be presented based on measured material parameters, and will be applied to determine both realistic and ideal conversion efficiencies attainable.

EM-TuP11 Characterization of the Electronic Structure of Dye-Sensitized Solar Cells, *S. Gutmann, M. Wolak, M.M. Beerbom,* ***R. Schlaf***, University of South Florida

The electronic structure of the interfaces in dye-sensitized solar cell structures was investigated using x-ray and ultraviolet photoemission spectroscopy (XPS, UPS). Electrospray thin film deposition in high vacuum was used to build the interfaces of interest directly in vacuum without exposure to the ambient. Electrospray enables the fabrication of clean, essentially uncontaminated thin films of organic molecules and nanoparticles directly in vacuum.

The experiments focused on the investigation of the indium tin oxide (ITO)/nanocrystalline TiO$_2$ interface, as well as the characterization of the

$TiO_2/RuL_2(NCS)_2$ [cis-bis(4,4'-dicarboxy-2,2'-bipyridine)–bis(isothiocyanato)-ruthenium(II)] ("N3", a prototypical dye used in many currently pursued device structures)-dye interface. Both TiO_2 and N3 films were built up in several steps. After each step, characterization by XPS and UPS was performed. The resulting sequence of spectra allowed the determination of charge injection barriers and interface dipoles at the ITO/TiO_2 and TiO_2/N3 interfaces. A particular focus of the experiments was the investigation of the influence of different surface conditions of the ITO on the electron injection barriers between TiO_2 and ITO.

EM-TuP13 Gas Sensing Mechanisms in Sub 6nm Thick Heterostructure Organic Thin Film Transistors, ***J.E. Royer***, *S. Lee, C.N. Colesniuc, I.K. Schuller, W.C. Trogler, A.C. Kummel*, University of California, San Diego

Understanding vapor interactions with organic thin films is key to application of organic thin films in chemical sensing. Ultra-thin organic thin film transistors (OTFTs) fabricated using only 4 monolayers (4ML) of metal phthalocyanines (MPc) are model devices for studying sensing physics since analyte adsorption is almost entirely restricted to the air/MPc interface since adsorption within the grain boundaries is minimal. Even in ultra-thin MPc OTFT heterostructures the films are sufficiently thin that gas adsorption occurs primarily from interfaces instead of grain boundaries. In an ideal ultra-thin heterostructure, gas adsorption should occur only at the interfaces thereby creating carrier traps which alter the conduction in the OTFT channel. This was directly investigated using MPc heterostructure OTFT s. The response to isophorone doses for metal free phthalocyanine (H_2Pc) OTFTs and cobalt phthalocyanine (CoPc) OTFT s were compared to OTFT s fabricated with bilayer films (CoPc/H_2Pc and H_2Pc/CoPc). The sensitivity to isophorone is more than 5 times greater for H_2Pc OTFTs than CoPc OTFTs, and the desorption kinetics fit a single exponential decay for H_2Pc whereas a bi-exponential decay is required for CoPc. The heterostructure OTFT responses did not strongly correlate with the H_2Pc or CoPc OTFTs which suggests a combination of surface doping and adsorption at the H_2Pc/CoPc interface. This could lead to highly sensitive OTFT sensors based on multilayered MPc film structures.

EM-TuP15 Microstructural Analysis and Luminescent Study of Thin Film Zinc Germanate Doped with Manganese, *K.H. Yoon*, ***J.H. Kim***, Chungbuk National University, Korea

Thin films of zinc germanate doped with manganese (Zn_2GeO_4:Mn) were fabricated by radio frequency planar magnetron sputtering, and their microstructural characteristics and luminescent properties were studied. X-ray diffraction measurements showed that the as-deposited Zn_2GeO_4:Mn films were of amorphous structure in nature. Field emission scanning electron microscopy and grazing incidence x-ray reflectivity analyses revealed that the Zn_2GeO_4:Mn films had a smooth surface morphology. The Zn_2GeO_4:Mn films exhibited a high optical transparency in the visible wavelength region with the peak transmittance of 0.926, which is very close to the transmittance of the quartz substrate alone. The Zn_2GeO_4:Mn films became crystalline by the post-deposition annealing above 700 °C in air and the annealed films possessed a rhombohedral polycrystalline structure with a random crystallographic orientation of grains. The broad-band photoluminescence (PL) and cathodoluminescence (CL) emission spectra were obtained from the annealed films. The emission extends from 470 to 650 nm with a maximum at around 535 nm in the green range, which is accounted for by the intrashell transition of $3d^5$ electrons from the $^4T_1$ excited-state level to the $^6A_1$ ground state in the divalent manganese ions.

EM-TuP16 Evaluation of ITO Films Deposited by Pulsed Electron Deposition, *H. V Nampoori, V. Rincon*, ***M. Chen***, *S. Kotru*, University of Alabama

Transparent conducting oxides (TCO) are the materials which combine visual transparency with high electrical conductivity. TCO films such as Indium Tin oxide (ITO) find its applications in photovoltaics, flat panel displays, electrochromic devices etc. ITO films are commonly grown by sputtering technique and presently meet current needs and quality for device applications. However, to achieve such good quality films, the films are grown at elevated substrate temperatures. This work explores a relatively newer vapor deposition technique known as pulsed electron deposition (PED) for the growth of ITO films where the films are deposited at room temperature. A commercially available target of ITO (90/10) was used as the source material. Films were deposited on soda lime glass and on Si (100) substrates. The oxygen pressure in the chamber during growth was varied from 2.8 mTorr to 22 mtorr. All the films were deposited for 5000 pulses. To evaluate the quality of grown films, various characterization techniques were employed. The optical transparency and the electrical conductivity of the films were found to be improving with increasing Oxygen pressure. Effect of Oxygen chamber pressure on resistivity, surface morphology, optical constants and carrier concentration on the films has been carried out. Details about the film preparation and evaluation of film properties will be presented.

EM-TuP17 Investigation of Oxide/InAs Interface via STM, STS, and KPFM, *W. Melitz*, ***J. Shen***, *A.C. Kummel*, University of California, San Diego

III-V MOSFETs have the potential to produce superior devices but formation of low defect density oxide-semiconductor interfaces is critical. While silicon surfaces are highly reactive due to their partially filled dangling bonds, some III-V surfaces have very low reactivity due to absence of partially filled dangling bonds and therefore might be able to form superior interface to high-k dielectrics if processes induce defect formation is avoided. Atomically resolved scanning tunneling microscopy (STM) and scanning tunneling spectroscopy (STS) were employed to determine the atomic and electronic structure of clean InAs surface and oxide/InAs semiconductor interfaces. Kelvin probe force microscopy (KPFM) can be utilized to support the STS and to provide further information on the surface or interface electronic properties. The InAs samples are first annealed at low temperatures to remove a protective arsenic cap, and heated to high temperature to prepare clean InAs(001)-(4×2) surfaces; the (4×2) surface is indium rich and therefore oxidation resistant which is favorable for oxide deposition. An oxide is deposited with a high temperature effusion cell and STS/KPFM measurements are performed to probe the surface Fermi level. SiO has the potential to form an excellent interface to ALD deposited HfO_2 since the Si/SiO_2/HfO_2 gate stack is known to have excellent electronic properties. STM images reveal that SiO forms cluster structures on the InAs(001)-(4×2) after annealing and does not desorb from the surface nor diffuse into the substrate after 800 K annealing. STS spectra for submonolayer SiO coverages deposited at 300 K on InAs(001)-(4×2) have shown the Fermi level is close to the conduction band for both n-type and p-type samples consistent with KPFM studies. For submonolayer SiO coverages deposited at 700 K on p-type InAs(001)-(4×2), STS shows the Fermi level near midgap consistent with partial unpinning; better electronic structure is expected for higher coverages of SiO. In_2O could act as a protection layer during high-k ALD and can be removed after ALD by high temperature annealing. STM images of In_2O deposited InAs(001)-(4×2) and annealed at 650 K show that In_2O forms has highly ordered structures. After annealing above 700 K, the In_2O desorbs from the surface and the pristine original clean InAs(001)-(4×2) is observed with no additional defects. Oxides are known to diffuse through HfO_2 and ZrO_2 so ALD deposition on In_2O could be followed by an annealing step which removes the In_2O to form a high-k/InAs without any ALD induced defects. STS and KPFM experiments on In_2O are ongoing.

EM-TuP18 Scaling Behaviors of Silicon Nitride Layer for Charge Trapping Memory, ***D.H. Li***, *I.H. Park, J.-G. Yun, J.H. Lee, D.-H. Kim, G.S. Lee, Y. Kim, S.H. Park, W.B. Shim, W. Kim, S. Cho, B.-G. Park*, Seoul National University, Korea

The scaling behaviors of silicon nitride, as charge trapping layer in embedded nonvolatile (poly) silicon-oxide-nitride-oxide-silicon (SONOS) flash memory application is presented. The conventional SONOS structure shows not only electron back-tunneling and charge retention loss problem, but also similar non-trapping behaviors at 5 nm silicon nitride thickness in our previous work. Therefore, we adopted an ultra thin oxide-nitride-oxide (ONO) barrier to replace the single tunnel oxide in the conventional structure and achieved enhanced memory characteristics. In this paper, we continuously investigate the limitation of scaling behaviors of silicon nitride for bandgap engineered charge trapping memory, according to dimension scaling down tendency in memory cells. The bandgap engineered device consists of multi-layer structure of oxide-nitride-oxide-nitride-oxide, which is fabricated by low pressure chemical vapor deposition (LPCVD). Memory characteristics, such as program/erase speed, and charge retention are characterized by *Quasi-steady static C-V* observation by Agilent 4156C and Agilent 41501B. Detected memory windows (ΔV_{FB}), which is defined as the change of flat band voltage from programmed state to erased state, are 3.32 V, 3.73 V, and 4.05 V, when Fowler-Nordheim (F-N) stresses is applied in 5 nm thickness of silicon nitride at -13 V, -12 V, and -11 V, respectively. These experimental data shows excellent memory operation behaviors, and indicates further scalability of charge trapping layer compared to the conventional structures. Device reliability issue is also evaluated by charge retention measurement. Experimental data demonstrates that device embodies excellent reliable memory operation.

Acknowledgements This work was supported by "Tera-bit Level Nano Device Project".

EM-TuP19 ESR Spectroscopy of VUV-irradiated HfO_2, *J.L. Lauer,* University of Wisconsin-Madison*, S.L. Cheng, B.B. Triplett,* Stanford University*, **J.L. Shohet**,* University of Wisconsin-Madison*, Y. Nishi*, Stanford University

We compare the charging response and defect generation, produced by vacuum ultraviolet (VUV) irradiation, of rapid-thermally annealed (RTA) 4nm thick HfO2 to as-deposited HfO2 on Si substrates. The HfO2 dielectrics were irradiated to 11.6 eV photons. The surface potential of the HfO2 samples was measured before and after VUV irradiation with a Kelvin probe system. The surface potential was determined to be negative before VUV irradiation and positive after irradiation for all samples except the 4nm thick HfO2 layer that was RTAd at 1000C. Paramagnetic defects within the HfO2 samples with and without VUV irradiation were measured with Electron Spin Resonance Spectroscopy (ESR). The VUV-irradiated samples indicate the presences of both E' and Ex centers. From VUV-spectroscopy, the valence-band structure and location of defects with the band gap of the HfO2 samples were determined and compared to density of states calculations to determine the origin of the electronic states measured. Initial results from VUV-spectroscopy suggest the presence of oxygen-interstitial defects (OID) located within the HfO2 layer and oxygen-deficient Si centers within the SiOx interfacial layer. We show the electronic states of OID in HfO2 line up in energy with oxygen-deficient Si centers within the SiO2 interfacial layer. We believe the oxygen-deficient Si centers are responsible for the accumulation of positive charge in the VUV irradiated HfO2 samples. We conclude that charge exchange between OIDs within HfO2 and the oxygen-deficient Si centers within the SiOx interfacial layer is very important for controlling the radiation-induced trapped charge in HfO2/SiOx/Si dielectric stacks.

Supported by the National Science Foundation under Grant Number DMR-0306582 and the Semiconductor Research Corporation under Contract Number 2008-KJ-1781. The UW Synchrotron Radiation Center is funded by the National Science Foundation under Grant Number DMR-0537588.

EM-TuP20 Annealing of ZrO_2 Thin Films Studied by Vacuum UV Spectroscopic Ellipsometry, *I. An, S. Lee,* ***H. Cheon****, J. Kyoung, H. Oh*, Hanyang University, S. Korea

ZrO_2 is one of the high-k dielectrics which can be used for the storage capacitor in dynamic random access memory devices. However, the physical properties of ZrO_2 films are highly dependent on the preparation process and conditions. Particularly, the thickness and temperature effects are most important. In this work, we investigated the annealing effect of ZrO_2 films which were prepared at various thickness ranges using atomic layer deposition. Vacuum ultraviolet spectroscopic ellipsometry (VUV SE) was employed to study the optical and microstructural properties of zirconium oxide (ZrO_2) films. Also XRD and capacitance measurements were performed. ZrO_2 films thinner than ~4 nm remained amorphous even at elevated annealing. Meanwhile thicker films developed into crystalline phases and the degree of crystallinity depended on the thickness.

EM-TuP21 Fabrication of Multilayer Thin Film Micro-Cooling Devices, ***K. Hedgeman****, M. Harris, Z. Xiao*, Alabama A&M University

Solid state thermoelectric cooling devices have been of current interest for hot-spot thermal management. Cooling hot-spots with high heat flux is becoming one of the most important technical challenges facing today's IC industry. The rising temperature limits device minimization and decreases its lifetime. In this paper, we report to fabricate in-plane and cross-plane solid-state thermoelectric cooling devices using multilayered Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ thin films. The Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ multilayer thin films were deposited using sputtering deposition. The Bi_2Te_3/Sb_2Te_3 and $Bi_2Te_3/Bi_2Te_{3-x}Se_x$ multilayer thin films have a periodic structure consisting of alternating Bi_2Te_3 and Sb_2Te_3 layers or Bi_2Te_3 and $Bi_2Te_{3-x}Se_x$ layers, where each layer is about 10 nm thick. The films were analyzed by XRD and SEM. The devices were fabricated using the standard integrated circuit (IC) fabrication process; pn junction diodes were fabricated as thermometers for the measurement of temperature in the devices. The fabricated in-plane and cross-plane multilayer thin film cooling devices and the achieved temperature difference from the cooling devices will be reported in the Conference. The developed devices could be a good candidate for the application of high-efficiency solid-state micro-cooling.

EM-TuP22 High-density Chalcogenide Nanostructure Arrays Fabricated by Self-aligned and Maskless Process with Modified Nanosphere Lithography, ***N. Kim****, H. Yang, H. Lee*, Chonnam National University, Korea

Phase change random access memory (PRAM) was concerned about one of the strongest candidate of non-volatile memory although the fabrication of PRAM has encountered the technical limitations by plasma process induced damage at sub-100 nm sizes. Novel approaches have been attempted to realize the reliability and utilization with a cost-effective production for high-density phase change memories. Nanosphere lithography (NSL) is one of the most useful techniques for the formation of close-packed periodic nanostructures. Polystyrene nanospheres of 500 nm-diameter were arrayed orderly on the photoresist (PR)-covered bottom electrode after dipping the samples into the developer solution for a few seconds to make the PR surface hydrophilic enough. The polystyrene nanospheres-arrayed samples were exposed. Then, polystyrene nanospheres were removed by DI water in an ultrasonic bath before development of PR. The average diameter of holes was about 100 nm. $Ge_2Sb_2Te_5$ (GST) was subsequently deposited into the periodic nanoholes, and then PR was lifted-off. High-density chalcogenide arrays were simply and successfully established by the self-aligned and maskless process of NSL. Acknowledgement: This work was supported by Korea Research Foundation Grant (KRF-2007-412-J02003).

EM-TuP23 Investigation of Crystal Structure and New Ellipsometric Properties of Hexagonal CdS Epilayers, ***D.J. Kim****, Y.D. Choi,* Mokwon University, Korea*, J.W. Lee,* Hanbat National University, Korea*, J.C. Sur*, Wonkwang University, Korea

High quality hexagonal CdS epilayer was grown on GaAs (111) substrates by the hot-wall epitaxy method. The crystal structure of the grown CdS epilayers was confirmed to be the hexagonal structure by X-ray diffraction pattern (XRD) and scanning electron microscopy (SEM) image. To explore binding states and their potential applications, the hexagonal structured CdS epilayers have been characterized using x-ray photoelectron spectroscopy (XPS). The optical properties of the hexagonal CdS epilayers were investigated in a wide photon energy range between 2.0-8.5 eV using spectroscopic ellipsometry (SE) at room temperature. The data obtained by SE were analyzed to find the critical points of the pseudodielectric function spectra, $< \varepsilon (E)>=< \varepsilon_1(E)>+i< \varepsilon_2(E)>$, such as E_0, E_{1A}, E_{1B}, E_0', F_1, and two E_2 structures. In addition, the second derivative spectra, $d^2\varepsilon(E)/dE^2$, of the pseudodielectric function of hexagonal CdS epilayers were numerically calculated to determine the critical structures. Four structures, such as E_0', F_1, and two E_2 structures, from 6.0 eV to 8.0 eV were observed, for the first time, at 300 K by ellipsometric measurements for the hexagonal CdS epilayers.

EM-TuP24 A Study on the In-Situ Phosphorus-Doped epi-$Si_{1-x}C_x$ Growth for NMOSFET Application, ***J.-H. Yoo****, D.-K. Lee, D.-H. Ko*, Yonsei University, Korea

As the size of complementary metal oxide semiconductor (CMOS) technology devices scales down, studies on strained channel engineering using lattice mismatch have received considerable attention since conventional structures shows serious problems, such as the increase of leakage current and the decrease of channel mobility. Specifically, in order to improve the electron mobility in the channel for NMOSFETs, many researches about source/drain epi-$Si_{1-x}C_x$ are in progress because of the successful employment of source/drain epi-$Si_{1-x}Ge_x$ in PMOSFETs. However, due to the extremely low solid solubility of C in Si in thermodynamic equilibrium, it is difficult to grow epi-$Si_{1-x}C_x$ with x > 1 at %. Furthermore, thermal annealing processes for the electrical activation of source/drain implants after the epi-$Si_{1-x}C_x$ growth can easily precipitate C atoms out from the substitutional sites, causing the loss of stress and affecting the junction and transport properties. In-situ doped epi-$Si_{1-x}C_x$ can maintain the strained $Si_{1-x}C_x$ layers with heavy doping because the process need not contain ion implantation and activation annealing. In this paper, we investigated the formation and the thermal stability of in-situ Phosphorus doped epi-$Si_{1-x}C_x$ in order to apply these films to the source/drain region of the ULSI device. The native oxide on Si (100) wafers was completely removed by HF cleaning and 100 nm-thick Phosphorus doped $Si_{1-x}C_x$ films were immediately deposited by UHV-CVD. Disilane (Si_2H_6), monomethlysilane (SiH_3CH_3) and phosphine (PH_3) gases were used for Si, C and P sources, respectively. The strains of the $Si_{1-x}C_x$ layer were investigated by using HR-XRD. The microstructures were observed by using HR-TEM.

EM-TuP26 Photoinhibition of Conductance Switching by Cycloaddition Reactions between Adjacent Molecular Switches, ***M. Kim****, J.N. Hohman, S.A. Claridge,* The Pennsylvania State University*, H. Ma, A.K.-Y. Jen,* University of Washington*, P.S. Weiss*, The Pennsylvania State University

Directed assembly and subsequent photomodulation of anthracene-terminated phenylethynylthiolate molecules provide a means to control charge transfer in molecular switches. These fully conjugated molecules were selectively inserted as lone molecules, or in pairs, into defect sites of *n*-alkanethiolate monolayers on Au{111}. Control of the assembly and a fixed molecular conformation on the surface allow a regioselective [4+4] cycloaddition between adjacent anthracene moieties under ultraviolet illumination. This photodimerization breaks the delocalized π network of the anthracene, which results in a dramatic conductivity decrease, observed as a photomodulated “off” state. The reaction between molecules also reduces stochastic conductance switching.

Graphene Topical Conference
Room: Hall 3 - Session GR-TuP

Graphene Topical Conference Poster Session

GR-TuP1 Reduction of Graphene Oxide using Electron Beam Generated Plasmas, *M. Baraket*, *E.H. Lock, S.G. Walton*, Naval Research Laboratory

Graphene and graphene oxide are the subject of intense research because of their unique structural and electronic properties which are advantageous in a large number of applications including nano-electronic and sensing devices. The amount of oxygen present in graphene oxide sheets strongly modifies their properties. Processes aiming to the reduction of oxygen are a current research interest. Wet-chemical approaches have been successful, but these methods have critical drawbacks in terms of scalability and time consumption. Plasma-based processes are an attractive replacement. The electron beam generated plasma developed by the Naval Research Laboratory provides a unique low electron temperature (< 1 eV) plasma and thus any ions leaving the plasma will do so with low ion kinetic energies at substrates. This novel plasma processing technique allows surface modification without excessive etching or surface damage. Experimental investigation of the reactions between plasmas produced in different gases (Ar, CH_4 and/or H_2 mixtures) and graphene oxide in an effort to reduce the concentration of oxygen will be presented. Material characterizations (chemistry, surface energy and surface roughness) and in-situ plasma diagnostics (electron temperature, plasma density) will also be discussed. This work was supported by the Office of the Naval Research. M.B and E.L. appreciate the support of the National Research Council.

GR-TuP2 Covalent Immobilization of Graphene on Solid Substrate, *L.-H. Liu*, *M. Yan*, Portland State University

Graphene, a two-dimensional atomic thin layer of carbon nanostructure, has emerged as a unique nanoscale material with promising applications in various areas due to its excellent mechanical, electrical, thermal and optical properties. Recently, much attention has been focused on graphene based devices. There is a growing need for developing new, simple, and cost-effective techniques to obtain stable graphene sheets on substrate. We present a simple and efficient method to covalently immobilize graphene on silicon wafers. Large graphene sheets were covalently attached to functionalized wafer surface by a simple heat treatment under ambient condition. The formation of single and multiple layers of graphene were confirmed by Raman spectroscopy, optical and atomic force microscopy. Evidence of covalent bond formation was given by X-ray photoelectron spectroscopy and solvent sonication treatment. In addition, this method can be readily applied to other substrates. This provides a facile approach to the construction of graphene-based integrated circuits on a wide range of substrates. The method offers immense opportunities to investigate how surface and interface chemistry affect the electronic properties and performance of graphene-based electronic devices.

References:

1. Geim, A. K., Novoselov, K. S. *Nat. Mater.* **6** (3), 183-191 (2007).

2. Gilje, S., Han, S., Wang, M., Wang, K. L., Kaner, R. B. *Nano Lett.* **7** (11), 3394-3398 (2007).

3. Park, S., Ruoff, R. S. *Nat Nano*tech. **4** (4), 217-224 (2009).

4. Liang, X., Fu, Z., Chou, S. Y. *Nano Lett.* **7** (12), 3840-3844 (2007).

5. Li, D. S., Windl, W., Padture, N. P. *Adv. Mater.* **21** (12), 1243-1246 (2009).

6. Yan, M., Ren, J. *Chem. Mater.* **16** (9), 1627-1632 (2004).

7. Liu, L., Engelhard, M. H., Yan, M. *J. Am. Chem. Soc.* **128** (43), 14067-14072 (2006).

GR-TuP3 Edge Structures of Graphene Nano-Patches Grown on the 6H-SiC(0001) Surface, *I. Kim, C. Hwang*, ***W. Kim***, Korea Research Institute of Standards and Science, Republic of Korea

Graphene nanoribbons (GNR) are currently considered as one of the most promising materials for future nanoelectronic devices due to its exceptional physical properties . We investigated the possibility of the growth of GNR on the vicinal 6H-SiC(0001) surface using Scanning Tunneling Microscopy. We observed the formation of the ribbon-like single-layer graphenes with sharp edge structures at the initial stage of thermal graphitization process of the SiC(0001) surface. However, the overall long-range ordering of the steps of the bare vicinal surface was found out to be lost during graphitization process, and only the local short range ordering of the steps with graphene layer patches existed on the entire surface. From the atom-resolved STM images, we clearly identified the armchair and zigzag edge structure for several ribbon-like graphene nanostructures, and found out that the zigzag structure were more frequently observed than the armchair structure. Scanning tunneling spectroscopy experiment was also carried out over the graphene nano-patches to examine the local electronic states at the edge structures.

GR-TuP4 Graphene on Demand, *P. Sessi,* Politecnico di Milano, Italy, *J.R. Guest, M. Bode*, ***N.P. Guisinger***, Argonne National Laboratory

The ultrahigh vacuum (UHV) scanning tunneling microscope (STM) has been utilized for controllably patterning regions of pristine graphene at the nanometer scale from an otherwise hydrogen saturated surface. We have found that the hydrogen saturation of graphene epitaxially grown on 4H:SiC(0001) is stable at room temperature and completely alters the original electronic properties which are no longer graphene-like. In addition to characterizing the structural and electronic properties of the surface at the atomic-scale, we have utilized the STM as a patterning tool via electron stimulated desorption of hydrogen, leaving behind regions of graphene. The STM enables a significant level of control and subsequent characterization of the graphene patterns at the highest resolution. With spectroscopic techniques we are able to extract electronic information of the patterned graphene regions. For patterned regions that are roughly 20 nm or greater, the inherent electronic properties of graphene are completely recovered. Below 20 nm we start to see dramatic variations in the electronic properties of the graphene as a function of pattern size.

Nanometer-scale Science and Technology
Room: Hall 3 - Session NS-TuP

Nanometer-scale Science and Technology Poster Session

NS-TuP1 Capture and Characterization of Nanoparticles at Trace Levels in Semiconductor Process Gases, ***J. Feng***, *M. Raynor, D. Davia, A. Seymour, R. Torres*, Matheson TriGas Inc.

Particulate contamination in process gases used in semiconductor fabrication can have harmful effects on device morphology, performance, reliability and yield. There are significant challenges in the measurement of particles in process gases, especially trace level nanoparticles <50 nm in reactive and corrosive gases. Optical particle counters and condensation nucleus counters are frequently used in inert gases to provide real time data on particle levels and size distributions. However these devices may not provide accurate size measurement or be compatible with reactive gases. Further, they don’t give any information on the composition of the particles, which may be important for determining the contamination source. An alternative method is to capture the particulate contamination on sampling filters and perform post microscopic analysis. This approach has been previously used for environmental particulate sampling but has not been widely applied to reactive semiconductor gases. In this work, a sampling system with nanopore-sized (NPS) membrane filter for capturing particles from difficult-to-measure gases is described, initially tested with a nanoparticle source in nitrogen and then applied to reactive process gases such as HBr. Feasibility of capturing iron oxide nanoparticles (30-50 nm) introduced into purified nitrogen via a particle shaker inert gas was demonstrated on NPS alumina filter. Sampling with HBr required compatibility testing of the filter membrane. Results indicated that the NPS alumina filter is capable of withstanding the corrosive effects of HBr, provided the sampling system and gas are properly dried. Membranes were analyzed using various surface analysis techniques such as AFM and SEM. Before collecting samples, blanks were collected to ensure that the delivery system was clear of any contamination. Typical results of contaminant particles from reactive gases such as HBr are presented. These data provide information on the particle content and form in the source container and delivery lines and efficiency of filters in removing particles from the flowing gas. SEM images of particles captured from a filtered gas sources via a delivery system show the presence of clusters of small particles, indicating that the particles may have an affinity for one another in the gas phase. SEM-EDS provides compositional data of the particles detected. The data show that in the case of HBr, the particles are mainly mixed metal bromides. The elements detected compare well to those detected by hydrolysis metal sampling with ICP-MS. Such information can assist in locating the source of particles and eliminating such sources

NS-TuP4 Large area Room-Temperature Nanoimprint using Liquid-phase HSQ Resin with PDMS Mold, ***Y. Kang***, *M. Okada, Y. Haruyama, K. Kanda, S. Matsui*, University of Hyogo, Japan

Nanoimprint lithography (NIL) is a very useful technique to make nanostructure devices with low cost and high throughput. So far, we reported room-temperature NIL (RT-NIL) using hydrogen silsesquioxane (HSQ) as a resin. However, the issue of a higher imprinting pressure than those of thermal NIL and UV NIL still remain to be addressed in NIL using spin-coated HSQ as the replication material. We attribute these disadvantages to evaporation of the solvent contained into HSQ during the spin-coating.

To overcome the above problem, we reported a Nanoimprint technique using liquid-phase HSQ as a replication material alternative to HSQ resin formed by conventional spin-coating. A low imprinting pressure and HSQ residual layer with less than 10 nm thick were achieved by using liquid-phase HSQ. But the HSQ-coated substrate is required to heat up around 90 ºC to evaporate the solvent contained in the HSQ resin while the pressure was held. And a large area imprinting was difficult because the organic solvent in the HSQ evaporated only through the side-gap between SiO$_2$/Si mold and HSQ coated Si substrate. To address these problems, we used Poly(dimethyl siloxane) (PDMS) mold instead of SiO$_2$/Si mold. Because PDMS is a porous gel, the organic solvent in the HSQ solution can be evaporated through PDMS mold.

The new imprint technique using liquid-phase HSQ with PDMS mold is as follows. First, the PDMS mold was fabricated by spin-coating a mixture of base resin and hardener resin (Dow Corning Co. Sylgard 184) on the SiO$_2$/Si master mold. Following, PDMS coated substrate was baked at 70 ºC for 15 min to cure the PDMS. After curing of the PDMS, the PDMS mold was demolded from the SiO$_2$/Si master mold. Next, HSQ solution was dropped onto a Si substrate. Following, the PDMS was pressed onto the Si substrate with 1MPa pressure. And then, the organic solvent in the HSQ solution was evaporated through the pores of PDMS. The imprinting temperature, pressure and time were RT, 1MPa, and 10 min, respectively. In this experiment, we used two kinds of HSQ, one is the caged HSQ (Dow Corning Co. Fox-16) and another is the ladder HSQ (Tokyo Ohka Kogyo Co. OCD T-12). Finally, the PDMS mold was removed from the Si substrate, and then HSQ patterns were successfully replicated on a 4 inch wafer in full area.

NS-TuP5 Electron Microscopy Characterization of Hexagonal Molybdenum Trioxide (MoO$_3$) Nano-Rods, ***I.B. Troitskaia***, *V. Atuchin,* Institute of Semiconductor Physics, Russia, *G.C. Franco,* University of Texas at El Paso, *D.A. Ferrer,* University of Texas at Austin, *M.A. Ramos, C.V. Ramana*, University of Texas at El Paso

MoO is an interesting material for application in solid state microbatteries,electronic information displays, and optical memory and sensor devices. MoO$_3$ exhibits several polymorphs and, hence, the controlled growth and structure of MoO$_3$ are highly important. The successful efforts to synthesize metastable hexagonal phase (*h*–MoO$_3$) have been very limited, partly due to the complications in stabilizing the metastable-phase as compared to the thermodynamically stable a -MoO$_3$. As such, the physicochemical properties of the metastable *h*–MoO$_3$ phase are largely unknown, in spite of the fact that metastable structures often demonstrate new or enhanced activity when compared to thermodynamically stable phases. Here, we demonstrate a simple low-temperature chemical method to produce metastable *h*-MoO$_3$ nanorods and their excellent structural characteristics. Hexagonal MoO$_3$ samples were prepared via the precipitation of molybdenum oxide from an ammonium paramolybdate solution, by the addition of nitric acid. The structure of *h*-MoO$_3$ nano-rods was examined in detail using high-resolution scanning electron microscopy (HR-SEM) and high-resolution transmission electron microscopy (HR-TEM). A drop of the nanorods diluted in ethanol was added onto a carbon-coated TEM grid, and allowed to evaporate for analysis on a FEI Tecnai TF20 (200kV) equipped with a STEM unit, high-angle annular dark-field (HAADF) detector and X-Twin lenses. The SEM data reveal that the nano-rod *h*-MoO$_3$ crystals have the shape of straight hexagonal rods with an aspect ratio ~60. The HR-TEM results confirm the hexagonal structure of the MoO$_3$ nanocrystals. Computations of the observed TEM data along with x-ray diffraction pattern further confirm the stability of the nano-structure of *h*-MoO$_3$ rods. The results obtained are presented and discussed.

NS-TuP6 A Photochemically Initiated Chemistry for Coupling Underivatized Carbohydrates to Gold Nanoparticles, ***X. Wang***, Portland State University, *O. Ramström,* KTH - Royal Institute of Technology, Sweden, *M. Yan*, Portland State University

Biofunctionalized metal nanoparticles provide a sensitive platform for the analysis and detection of molecular recognitions in biological system. The remarkably sensitive optoelectronic properties of metal nanoparticles make nanoparticle-based materials a powerful tool to study fundamental biorecognition processes. Here we present a new and versatile method for coupling underivatized carbohydrates to gold nanoparticles (Au NPs) via the photochemically induced reaction of perfluorophenylazide (PFPA). A colorimetric model system based on the carbohydrate-modified Au NPs was furthermore constructed for the sensitive detection of carbohydrate-protein interactions. Treating mono-, and di-mannose-modified Au NPs with Concanavalin A (Con A) lead to a distinct color change of the Au NP solution, which was directly associated with the surface plasmon resonance shift upon nanoparticle aggregation. The coupling chemistry is highly efficient and is applicable to a wide range of carbohydrate structures.

NS-TuP7 Fabrication of Quantum Dots Utilizing Multi-Coated Self-Assembled Monolayer, ***N.Y. Kwon***, *K.H. Kim, I.S. Chung*, Sungkyunkwan University, Korea

We have created various nano-gaps by controlling the number of self-assembled molecular coating. The generated nano-gaps were used to yield quantum dots with a precise size and placement. First, Au electrodes with an unique shape were obtained using a conventional lithography. Then, self-assembled multilayer, composed of alternating layers of α, ω - mercaptoalkanoic acids (~2 nm) and copper (II) ions, were deposited on Au electrode patterns to form the controllable gap between adjacent Au electrodes. After reaching to nanometer-scale gap, the secondary Au was deposited again and lift-off both ZEP420A(E-beam resist) and molecular resist, thereby resulting in quantum dot with nano-gap between gold electrodes. Ellipsometry and cyclic voltammetry (CV) were used to analyze the number of self-assembled molecular layer. Also, contact angle and X-ray photoelectron spectroscopy (XPS) were used to analyze chemical properties between gold and self-assembled multilayer. Additionally, Scanning probe microscopy (SPM) and field emission secondary electron microscopy (FE-SEM) were used for characterization on shape of nano-gap and quantum dots.

NS-TuP8 The Efficient Film Growth Method for Active Layer of Polymer Solar Cells, ***K.W. Kim***, *H.J. Kim, B.Y. Hong*, Sungkyunkwan University, Korea

Polymer based organic solar cells have made rapid progress after the advent of bulk-heterojunction concept consisting of an interpenetrating network of electron donor and acceptor material. Since slow growth of active layer allows to improve the cell performance, some approaches have been already used to reduce the film growth rate such as boiling point modification using solvent mixture, slow drying or solvent annealing by reducing spin coating time which controls the solvent annealing time.

In this work, we investigate the role of spin coating frequency combined with solution concentration at fixed active layer thickness on performance of polymer solar cells based on regioregular poly(3-hexylthiophene) (RR-P3HT):[6,6]-phenyl-C61–butyric acid methyl ester(PCBM) system. The thickness of active layer is standardized by controlling the solution viscosity with solution concentration. It is found that the spin coating frequency is associated with solvent evaporation time and highly affects the degree of interpenetration of the crystalline P3HT and the highest power conversion efficiency was obtained with the combination of the possible lowest spin coating frequency and solution concentration under AM 1.5 G spectral illumination of 100 mWcm^{-2}. The structural and optical properties of active layer are characterized by various analysis methods such as X-ray diffraction (XRD), ultraviolet-visible absorption spectroscopy and atomic force microscopy (AFM).

NS-TuP9 Study on Inverted Hybrid Solar Cell with ZnO Thin Film for Stability Improvement, ***J.W. Park***, *Y.S. Park, B.Y. Hong*, Sungkyunkwan University, South Korea

Recently, the organic solar cell has been receiving lots of attention as a clean and safe energy source instead of the fossil fuel due to its lower manufacturing cost and environment-friendly energy conversion capability. Several research groups have claimed the organic solar cells with ~5 % conversion efficiency. However, they still have low efficiency and the unstable because organic materials are easily oxidized by humidity and UV light under the atmosphere environment.

In this work, we propose an inverted-type organic/inorganic hybrid solar cell using ITO/ZnO/P3HT:PCBM/Au (indium tin oxide/zinc oxide/poly(3-hexylthiophene) : [6,6]-phenyl C$_{61}$ butyric acid methyl ester/Au) structure to enhance the efficiency and the stability of the organic solar cell. ZnO thin film is used as buffer layer to prevent the interface of organic layer by UV light from the oxidation and to reduce the energy barrier for easily transferring electron between ITO electrode and the LUMO level of the organic acceptor. Also, ZnO film blocks the injection of the hole from the P3HT to ITO for no charge carrier recombination. It is observed that the power conversion efficiency is significantly dependent on the thickness of ZnO thin film, which is deposited with magnetron sputtering system. The power conversion efficiency of 2.6 % under AM 1.5 G spectral illumination of 100 mWcm^{-2} is obtained when the thickness of ZnO thin film and P3HT:PCBM is optimized. In addition, Au used as back electrode to solve the problem of Al, which is susceptible to reactions with oxygen and water, and to control the work function between HOMO level of P3HT and the energy level of metal electrode. From the periodically testing result for long days, we proved that our solar cell which isn't encapsulated has a longer stability than typical organic solar cell fabricated by the same condition under ambient.

NS-TuP10 Growth of Vertical Si Nanowires Using Square Matrix Anodic Aluminum Oxide Template

J.K. Hong, *K.H. Kim, J.H. Heo, I.S. Jung*, Sungkyunkwan University, Korea

The vertical Si nanowires were grown on Si(100) substrate using a low-pressure chemical vapor deposition(LPCVD) system. The square pattern of AAO was obtained by combining pre-patterning Al thin film surface using focused ion beam (FIB) with anodizing process. The pore size and its period of the square matrix were approximately 50nm and 100nm, respectively. To determine the role of the indent depth on Al surface in AAO formation, FIB doses were varied from 1x10^{17} ions/point to 8x10^{17} ions/points. We found that a minimum indent depth is about 16nm. The minimum indent depth seems to be required to localize electric fields in a downward direction thereby yielding an indented pattern after AAO formation. In addition, we found that the higher voltage in anodizing process yields better uniformity in pore shapes. The Au nanoparticles as the catalyst for epitaxial growth of Si nanowires were deposited at the bottom of the AAO template on Si substrate using a electroless deposition with a mixuture of a solution containing Au ions and 1% HF. The average diameter of Au nanoparticles in each pore was 65nm.

The physical properties were analyzed using secondary electron microscope (SEM), transmission electron microscopy (TEM), and X-ray diffraction. Additionally, the detailed analysis including pore diameter and pore depth were made using scanning probe microscope (SPM).

NS-TuP12 Nanostructuring by Ion Beam: The Role of Surface Active Elements

B. Setina Batic, *M. Jenko*, Institute of Metals and Technology, Slovenia

Ion bombardment has recently attracted much attention as a tool for inducing self-organized patterns on various metal, semiconductor and amorphous surfaces. Depending on the conditions imposed upon the ion beam as well as on the properties of the material, different surface morphologies can form. The most common surface topography that forms under the ion beam influence is ripple-like morphology, which is prevalent in the case of amorphous materials, but in the case of semiconductors and single crystalline metal materials observations of dots, pits, mounds and pyramidal structures have also been documented.

Polycrystalline Fe-3%Si alloy was chosen as a model system for studying sputter induced topography modulations due to its properties: each grain, ranging few µm in size and of different crystalline orientation, behaves as a single-crystal surface that sputters independently of the surrounding grains. Thus, it is possible to experimentally include a large amount of grains of different crystallographic orientations in the same experimental run. Additionally, the samples were doped with a small amount of surface active elements to verify their role on the formation of self-assembled structures.

Samples of Fe-3%Si alloy were polished to achieve a smooth starting surface and subjected to Ar+ ion beam irradiation of different energy, angle and ion dose to obtain a complete set of experimental data on ion induced morphology changes. Results show that the surface exhibits grain-orientation dependent patterns, ranging from well-defined ripple structures to terraces, pits, or pyramidal structures. The characteristic length of these structures is in the order of a few hundred nanometres. Preliminary results show that surface active elements, such as Se or Sn, have a determining role on the formation of ripple-like patterns, causing the ripples to develop facet-like characteristics.

The samples were characterized using a multitechnique approach: Field Emission Scanning Electron Microscope (FE-SEM, Jeol JSM 6500-F) was used for the determination of different structures that formed in individual grains and to visualize a larger area of the sample, while Atomic Force Microscope (AFM, Veeco) gave detailed information on corrugation, individual ripple wavelengths, facet angles, pit depths and other morphological details.

NS-TuP13 Photo-patterning of Nitrophenyl-Terminated Self-Assembled Monolayers by using Localized Surface Plasmon

S. Uenishi, *T. Ichii, K. Murase, H. Sugimura*, Kyoto University, Japan

Patterning of self-assembled monolayers (SAMs) has attracted much attention owing to its potential applications to various microdevices fabrication processes. In particular, photochemical micropatterning of SAMs is of special interest, since it can be adopted into photolithography which has been the most successful microprocessing technology with high productivities. Recently, photoinduced reduction of nitrophenyl-terminated SAMs on silver surfaces has been reported [1], where nitrophenyl groups were converted to phenylamine groups by visible light irradiation. This must be prominently useful technique in the field of biotechnology and photochemistry, because some biomolecules and nanoobjects of noble metals can be adsorbed on amino-terminated surfaces. However, visible light irradiation is difficult to be applied to nanoscale patterning owing to diffraction limit. This can be overcome by using localized surface plasmon with nanoobjects of noble metals. Electromagnetic field relative to the surface plasmon is localized in a few tens of nanometer, which is independent of light wavelength. In this study, we demonstrated photoinduced reduction from nitrophenyl groups to phenylamine groups by using direct light irradiation and localized surface plasmon.

First, 4-nitrobenzenthiol (NBT) SAMs were irradiated with visible light through photomask. The SAMs were formed on gold substrates by immersing the substrate in ethanol solution of NBT (1 mM) at room temperature for 24 hours. Photochemical changes were detected as surface potential shift using Kelvin-probe force microscopy. The surface potential of the irradiated regions was positively shifted by approximately 10 mV. This potential change suggests some photochemical changes induced by the light irradiation on the SAM. Water contact angle measurement and X-ray photoelectron spectroscopy (XPS) were also applied to the SAMs which are irradiated with the light through plain glass plate in these cases. Water contact angle increased from about 45 degrees to about 50 degrees after visible light irradiation. Proof of the photoinduced reduction was not detected by the XPS measurement probably because X-ray irradiation also promoted reduction of the nitrophenyl groups. These results suggest some changes induced on the surfaces by the light irradiation.

[1] M. Naoki, S. Takahiro, O. Masatoshi and U. Isamu, Chemistry Letters, 24, 145 (1994).

NS-TuP14 Enhanced Thermal Stability and Nanoparticle-mediated Surface Patterning: Pt/TiO$_2$(110)

F. Behafarid, *A. Naitabdi, B. Roldan Cuenya*, University of Central Florida

Size-selected Pt nanoparticles were synthesized by inverse micelle encapsulation on PS-PVP diblock copolymers. The thermal stability of these Pt nanoparticles deposited on TiO$_2$(110) has been investigated by scanning tunneling microscopy. Our micelle-based nanoparticles were found to be very stable against agglomeration and they preserved their initial size (~3.2 nm) and hexagonal arrangement up to an annealing temperature of at least 1000°C [1]. Furthermore, the original spherical shape of these particles was found to change upon annealing above 1000°C, leading to the formation of 3D faceted particles. Atomic desorption and cluster coarsening was observed at 1060°C. Our study also revealed that strong nanoparticle/support interactions are present in this system, resulting in the formation of TiO$_2$ nanostripes at high temperature with widths and a 2D spatial arrangement pre-determined by the presence and distribution of the Pt nanoparticles on the substrate.

Further insight into the mechanisms underlying the enhanced thermal stability of our micellar nanoparticles was obtained via a comparative study with UHV-evaporated Pt nanoparticles supported on pristine and polymer-coated TiO$_2$(110) surfaces.

NS-TuP15 STM Measurements at mK Temperatures for Higher Energy Resolution

Y.J. Song, A.F. Otte, NIST and University of Maryland, College Park, ***Y. Kuk***, NIST and Seoul National University, Korea, *J.A. Stroscio*, National Institute of Standards and Technology

Since the invention of scanning tunneling microscopy (STM) in early 1980's, STM and STM-based measurement techniques have been used in a variety of fields for their atomic resolution. With the advent of cryogenic microscopes operating around 4K, the high resolution spectroscopic capabilities of the STM have had significant impact. In this poster, we describe our efforts to make STM measurements at even lower temperatures approaching 10 mK to gain further energy resolution in spectroscopic measurements. To realize this enhanced energy resolution, we constructed an ultra high vacuum (UHV) Dilution Refrigerator (DR) based STM system. The DR was constructed very rigidly in order to have a high resonance frequency. Furthermore, it has two independent modes of He3-He4 mixture gas condensation: a traditional 1K pot condenser, and a Joule-Thomson condenser for possible lower noise operation. For STM measurements, we custom-designed and built an STM module suitable for operation at mK temperatures. The whole STM module can be transferred from the upper, room-temperature chamber where the sample and tip can be easily exchanged. The sample holder has five isolated electrical contacts which are also used for kinematic mounting of the sample. This allows four-probe electrical measurements to be performed simultaneously with STM measurements. A cryogenic current amplifier has been constructed and is mounted in the DR for low noise tunneling measurements. We describe the current progress and performance of this new system.

NS-TuP16 A Probe Characterizer for Atomic Force Microscope Fabricated from Si/SiO$_2$ Multilayers, ***H. Itoh***, AIST, Japan

A method to fabricate accurate nanostructures was developed using supperlattices and selective etching technique [1]. A probe shape characterizer for atomic force microscope (AFM) was developed for reliable measurement of AFM image and ISO standardization [2]. Comb-shape lines and spaces (10 nm to 50 nm) were fabricated using Si/SiO$_2$ superlattice. Line width and space distances were determined from the crossectional image of transmission electron microscope. Edge radii of these structures were less than 1.5 nm, and line width and line distance were fabricated in the accuracy less than 1.5 nm. The comb-shape lines and spaces were used to determine the aspect ratios of the AFM probe shape [1]. Aspect ratios of cone-like probe from tip apex to the bottom can be determined from apparent depth in the AFM image obtained from 8 kinds of different space widths. In case of the CNT probe, diameter of cylinder-like probe can be estimated from trajectory of the AFM probe on space structure. Advantage of characterizing probe shape using comb-shape pattern is that uncertainty can be defined from the shape of the reference material. Thus, reconstructed AFM image is reliable and applicable to characterize the precise morphology of nano-materials [3] and nano-structures.

References

[1] Hiroshi. Itoh, Toshiyuki. Fujimoto, and Shingo. Ichimura, Rev. Sci. Instrum. 77, 103704, (2006).

[2] Daisuke Fujita, Hiroshi Itoh, Shingo Ichimura and Tomizo Kurosawa, Nanotechnology 18, 084002 (2007).

[3] Hiroshi Itoh, Chunmei Wang, Yoshikazu Homma, Jielin Sun, Jun Hu, Shingo Ichimura, JJAP 47, 6128 (2008).

NS-TuP17 Growth and Optical Properties of ZnO Fern-like Nanoleaves, *H. Ji*, Jilin University, P.R. China, ***H. Gao***, Harbin Normal University, P.R. China, *Y. Zhao*, Northeast Forestry University, P.R. China

Zinc oxide is a very widely studied nanomaterial due to its potential applications in nanoscale optoelectronic and photovoltaic devices. A variety of ZnO quasi-one-dimensional morphologies have been synthesized by different methods. Often applications of the ZnO nanostructures are closed related to their morphology providing motivation to study the relationship between the morphology and growth technique.

Using a mixture of ZnO, Eu$_2$O$_3$ and C powder as source material, ZnO with a novel morphology referred to as nanoleaves was fabricated using thermal evaporation. The structures and morphologies of the as-synthesized samples were characterized by x-ray diffraction, field-emission scanning electron microscopy, high-resolution transmission electron microscopy and energy dispersive x-ray spectroscopy. The ZnO nanoleaves are wurtzite single crystals that have an appearance of fern-like leaves w ith symmetrical paired teeth on opposite sides. For some of the nanoleaves, there are long needles that grow from the end of some of the teeth and forming parallel arrays. The growth mechanism, kinetically driven process and photoluminescence of the ZnO nanoleaves will be discussed.

NS-TuP18 Characteristics of Al-doped ZnO Film and its Application to the Electrode for Inverted Organic Solar Cell, ***D.H. Lee***, *S.U. Lee, B.Y. Hong*, Sungkyunkwan University, Korea

High-quality Al-doped zinc oxide (ZnO:Al; AZO) films are very attractive materials due to relatively low cost, non toxicity and stability at high temperature, and also they are being extensively investigated to apply to various fields such as solar cells, flat panel displays and organic light emitting diodes.

In this work, we investigated the electrical, optical and structural properties of AZO film grown on the glass by RF magnetron sputtering method with zinc oxide target doped Al$_2$O$_3$(2 wt%). AZO films were synthesized at the pressure of 1mTorr with RF power varied from 100 W to 175 W. The optimized AZO film had the transmittance above 85% at visible region and the resistivity of 1.5×10^{-3} ohm-cm at room temperature. The characteristics of AZO film were investigated by X-ray diffraction (XRD), Hall measurement system, UV-visible spectroscopy, and atomic force microscopy (AFM).

In addition, the optimized AZO film in this work was applied to a transparent electrode for an inverted organic solar cells (AZO/P3HT:PCBM/PEDOT:PSS/Au) which was compared with the organic solar cell with the standard structure using indium tin oxide (ITO) as the electrode.

NS-TuP19 Comparison of Oxidation Behaviors of Si$_{1-x}$Ge$_x$ Nanowires, ***S.Y. Kim***, *S.W. Kim, D.-H. Ko*, Yonsei University, Korea

Conventional devices came to have issues as scaling down. One of the methods to overcome the limit of scaling down is semiconductor nanowires and because of their potential application for nano-scale devices they have received considerable attention during the past years. Compared to other semiconductor nanowires, Si & Si$_{1-x}$Ge$_x$ nanowires are more important as for the base-materials of future nano-scale device because of their special merit of being compatible with current silicon device fabrication processes. In addition to this, Si & Si$_{1-x}$Ge$_x$ nanowires are suitable candidates for investigating characteristics associated with quantum size effects. Among the conventional Si-compatible processes, the oxidation properties are of great interests so we investigated the oxidation of Si$_{1-x}$Ge$_x$ nanowires at the point of Ge behaviors during oxidation. Si$_{1-x}$Ge$_x$ nanowires were grown in a LPCVD by VLS method. Source gases of SiH$_4$ and GeH$_4$ were used for growing Si$_{1-x}$Ge$_x$ nanowires on Si (111) substrates. Thin gold layer was deposited as catalyst, and Ge contents of Si$_{1-x}$Ge$_x$ nanowires were controlled to 15% and 30%. Grown nanowires were thermally oxidized in the vertical furnace with the various temperature and time. After oxidation, grown oxide thicknesses were measured by TEM methods and compositions of oxide and remain nanowires were analyzed by TEM and EDS methods. Comparing the oxidation characteristics of the Si$_{1-x}$Ge$_x$ nanowire with those of Si nanowires and (100) Si wafer, it is concluded that Ge plays a significant role in deciding an oxidation characteristics and oxidation characteristics of Si$_{1-x}$Ge$_x$ nanowires can be affected by Ge contents as well as nanowire size.

NS-TuP20 Carbon Nanotube Embedded Three Dimensional (3-D) Carbon Microelectrodes for Rechargeable Microbatteries, ***G.H. Kim***, *E. Kozarsky, H.S. Jee, K.T. Kim, J. Kim, E. Takeuchi, Y.-K. Yoon*, University at Buffalo

Lithium ion rechargeable batteries power a wide range of electronic devices including cell phones, laptop computers, digital cameras, and medical devices because of the high energy density. However, the technological development of the battery has been held back by the limited range of available electrode materials. Desirable battery electrodes are to have a large surface area for high energy density and device compactness, and a fast charging/recharging property for high power demand. Recently, three dimensional (3-D) carbon electrodes have been successfully demonstrated using the polymer carbonization process with lithographically defined high aspect ratio microstructures [1]. The advantages of this approach include the accurate definition of 3-D microstructures using ultraviolet (UV) lithography and converting them into the carbon electrode by pyrolysis, resulting in chemically and mechanically stable, low cost electrodes. However, the carbon electrodes from polymer pyrolysis show relatively high electrical resistivity resulting in slow charging/discharging response. On the other hand, carbon nanotubes (CNT) are known to provide outstanding electrical, mechanical and chemical performance.

In this study, we report carbon nanotube (CNT) embedded 3-D carbon electrodes by using UV lithography on CNT embedded SU8 (photosensitive negative tone epoxy) and subsequent carbonization. Since the final electrodes consist of CNTs embedded in pyrolyzed carbon, they contain high electrical conductivity to contribute to increasing charging/discharging speed and chemical, mechanical stability in the electrolyte environment. Also, the small amount of CNTs in polymer does not interfere much with UV dose in the photolithography process, maintaining the high aspect ratio 3-D micropatterning capability.

[1] G.T. Teixidor, R.B. Zaouk, B.Y. Park, M.J. Madou, "Fabrication and characterization of threedimensional carbon electrodes for lithium-ion batteries", Journal of power sources 183 (2008) 730-740.

NS-TuP21 Silicidation Behaviors of Si$_{1-x}$Ge$_x$ Nanowires for Future CMOS Device, ***S.W. Kim***, *S.Y. Kim, D.-H. Ko*, Yonsei University, Korea

To overcome the scaling down issues in current semiconductor industry, scientists and engineers have been investigating the alternatives in the last few years. One of the methods is a semiconductor nanowires. They have been received remarkable attentions during the past years due to their potential application for future CMOS devices. Compared to other semiconductor nanowires, Si & Si$_{1-x}$Ge$_x$ nanowires are more important as for the base-materials of future CMOS devices because of their special merits of being compatible with current silicon device fabrication processes. In addition, Si & Si$_{1-x}$Ge$_x$ nanowires are suitable candidates for investigating characteristics associated with quantum size effects. For the application to the future nano-scale device process, we investigated the silicidation behavior of Si$_{1-x}$Ge$_x$ nanowires. Si$_{1-x}$Ge$_x$ nanowires were grown in a LPCVD by VLS method. SiH$_4$ and GeH$_4$ were used as a precursor sources for growing Si$_{1-x}$Ge$_x$ nanowires on Si (111) substrates. Thin gold layer was deposited as a catalyst, and Ge contents of Si$_{1-x}$Ge$_x$ nanowires were controlled to 15% and 30%. Ni layer was deposited on the as-grown nanowires by sputtering and RTP process was used for silicidation. The characteristics of Ni germanosilicide films on nanowires were investigated by using TEM and EDS methods. Also, electrical characteristics were measured by using patterned electrodes. Comparing the silicidation characteristics of $Si_{1-x}Ge_x$ nanowires with those of Si nanowires, it is concluded that Ge plays a significant role to determine silicidation characteristics.

NS-TuP22 Electrospun ZnO Nanowire Based Ferroelectric Field-Effect Transistor using a Gate Dielectric Layer of $Bi_{3.25}La_{0.75}Ti_3O_{12}$ Thin Film, *K.T. Kim*, *G.H. Kim, Y.-K. Yoon*, University at Buffalo

Recently, ZnO nanowires (NWs) have been extensively studied for solar cell and field-effect transistor applications because of their intrinsic n-type semiconductor property with a wide band gap of 3.36 eV and a large exciton binding energy of 60 meV[1]. Specially, the nanowire architecture in field-effect transistors provides many advantages against the conventional bulk substrate approach such as device size reduction, isolated channel, reduced leakage current, reduced control voltage, and reduced power consumption even to several nJ[2]. The ZnO nanowire based transistor can be extended to a non-volatile memory device by adopting ferroelectric materials for the gate dielectric layer. While Bi-based perovskite $Bi_{3.25}La_{0.75}Ti_3O_{12}$ (BLT) and $Pb(Zr,Ti)O_3$ (PZT) thin films have been extensively investigated for non-volatile ferroelectric random access memory (FRAM) devices, BLT based devices are reported to offer better fatigue resistant characteristic, low processing temperature, and large remnant polarization.

In this study, we show a process to make ZnO nanowires using electrospinning with the polymer ZnO nanocomposite and subsequent sintering in various temperatures and characterize them. Also, BLT is prepared by the metal organic deposition (MOD) process and is spincoated on a Pt(150nm)/Ti(50nm)/SiO_2/Si substrate, followed by sintering in different temperatures (550°C, 600°C, 650°C, and 700°C) to form crystalline perovskite structures [3]. And the ZnO nanowires are formed on the BLT ferroelectric gate and the electrodes for source and drain are defined using a UV lithography followed by metallization. We show non-volatile switching in ZnO NWs with the BLT ferroelectric gate. We also evaluate the field dependent conduction of ZnO NWs with the remnant field of ferroelectric thin films and show fatigue and retention free performance. These devices are useful not only for non-volatile memory devices but also for various biosensors and nanoelectromechanical systems.

[1] B. Sun, and H. Sirringhaus, Nano Lett., 5, 2408(2005)

[2] X. Duan, Y. Huang, and C. M. Lieber, 2, *Nano Letters*, 487 (2002)

[3] Kyoung-Tae Kim, Chang-Il Kim, Yong-Kyu Yoon, " Characteristics of La-substituted Bismuth Titanate Ferroelectric Nanofibers by Electrospinning "AVS 55th Inter. Symp. Boston, USA (October 19-24, 2008)

NS-TuP23 Fabrication of n-ZnO Photonic Crystals by Nanosphere Lithography using Inductively-Coupled-Plasma Reactive Ion Etching with $CH_4/H_2/Ar$ Plasma on the n-ZnO/GaN Heterojunction LEDs, *S.J. Chen*, National Tsing Hua University, Taiwan, *C.-M. Chang, J.S. Kao,* Instrument Technology Research Center, National Applied Research Laboratories, Taiwan, *F.R. Chen, C.H. Tsai*, National Tsing Hua University, Taiwan

Applying photonic crystals with Light Emitting Diodes (LEDs) to improve the light extraction efficiency have been demonstrated successfully. ZnO has been considered as a promising material for the development of next generation UV LEDs with high brightness due to its direct band gap (3.37eV) at room temperature and it has relatively large exciton binding energy. Recently, n-ZnO/p-GaN heterojunction LEDs have been fabricated by several groups. However there has not any experimental evidence yet to integrate photonic crystal with n-ZnO/p-GaN heterojunction LEDs. This paper reports fabrication of n-ZnO photonic crystal/p-GaN LED by nanosphere lithography to further booster the light efficiency.

Usually, electron beam lithography is employed to fabricate the photonic crystals, however, it is a cost process and not suitable for large area production. In our paper, the fabrication of ZnO photonic crystals is carried out by nanosphere lithography (NSL) using inductively-coupled-plasma reactive ion etching (ICP_RIE) with CH4/H2/Ar plasma on the n-ZnO/p-GaN heterojunction LEDs. NSL is a simple and relatively cheaper technique and allows for large-area production. The $CH_4/H_2/Ar$ mixed gas gives high etching rate of n-ZnO film which yields a better surface morphology and results less plasma-induced damages of the n-ZnO film.

The periocity of n-ZnO photonic crystal is designed to fit the spectrum of n-ZnO/p-Gan LED by a Matlab code which suggests an optimum lattice parameter is 200 nm and the air-filling factor of the n-ZnO photonic crystal ranges from 0.35 to 0.65. In our paper we will show our recent result that a ZnO photonic-crystal cylinder has been fabricated by using polystyrene-nanosphere mask with lattice parameter of 200 nm and radius of hole around 80 nm. Experiment results were discussed in detail in terms of surface morphology , photonic-crystal nano-structure and plasma-induced damages which were measured by atomic force microscope, scanning electron microscope and photoluminescence spectrometer respectively.

NS-TuP24 Dielectrophoresis-assisted Deposition and Alignment of Single-Walled Carbon Nanotubes for Electronic Device Fabrication, *Z. Xiao*, Alabama A&M University

Single-walled carbon nanotubes (SWCNTs) have been considered as a promising nanostructured material for the realization of future nanoelectronic devices because of their unique electrical properties such as the ballistic transportation of electrons or holes in SWCNTs. In this paper, we report deposition and alignment of SWCNTs using the dielectrophoresis (DEP) method and fabrication of single-walled carbon nanotube field-effect transistors (CNTFETs) with semiconductor materials as the source and drain materials. Ultra-purified HiPCO-grown single-walled carbon nanotubes (SWCNTs) from Carbon Nanotechnologies, Inc. (CNI) were used for the fabrication of CNTFETs. N-Methyl Pyrrolidone (NMP) was used to disperse SWCNTs in solutions. The dispersion of SWCNTs in the solvent was ultrasonically assisted, and then centrifuged. The degree of dispersion was examined by SEM. Dielectrophoresis (DEP) method was used to deposit, align, and assemble carbon nanotubes (CNTs) across the source and drain of CNTFETs to form the channel. Microfabrication techniques such as UV lithography and e-beam lithography were used to fabricate the CNTFETs. The gap between the source and drain varied from 800 nm to 3 um. Both metals such as gold and semiconductors such as bismuth telluride (Bi_2Te_3) were used as the source and drain materials for the CNTFETs. The drain-source current (I_{DS}) versus drain-source voltage (V_{DS}) and gate voltage (V_G) was characterized for the fabricated CNTFETs. The fabricated devices and measured electrical results will be reported in the Conference.

NS-TuP25 Three-dimensionally Suspended Single-Walled Carbon Nanotubes Inside the Holes of Porous Silicon, *W. Yi*, *D. Lee, J. Lee*, Hanyang University, Korea

Carbon nanotubes (CNTs) were synthesized inside the holes of the porous silicon substrate by thermal decomposition of C_2H_2. Secondary electron microscopy (SEM) and Raman analysis revealed that single-walled carbon nanotubes (SWNTs) were suspended with three-dimensional networks (3-dim suspended SWNTs). Field emission measurements of those samples showed the enhanced turn-on voltage and emission property compared with pristine SWNT film. We also measured the photoconductivity of 3-dim suspended SWNTs under irradiation of infrared light after making two electrodes on the sample surface. The on/off ratio of resistivity, i.e. the resistance ratio under and without IR irradiation reached up to ~600 enough to be used as commercial IR sensors.

NS-TuP26 System Evaluation and Optimization of the Measurement Uncertainty in the Nanoscale Step-height Inspection by Dynamic Mode Atomic Force Microscopy, *C.Y. Su*, *Y.H. Lin, S.S. Pai, P.L. Chen, N.N. Chu, C.C. Yang, M.H. Shiao*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

Atomic Force Microscopy (AFM) has been extensively adopted in a variety of applications in nanotechnology. Due to the high sensitivity in z-axis, the capability of mapping height distribution from sample topography with the resolution in the sub-angstrom is achieved. In this study, a standard operation process (SOP) has been designed and implemented in order to optimize operational parameters such as scan rate, drive frequency, target amplitude, set-point, integral gain, proportional gain, look-ahead gain and so forth for the AFM dynamic mode inspection. The step-height standards are provided by the national metrology institute Physikalisch-Technische Bundesanstalt (PTB). System evaluation of the measurement uncertainty is accorded to ISO, Guide to the Expression of Uncertainty in Measurement and ISO 4287, Geometrical Product Specifications (GPS) - Surface texture: Profile method – Terms, definitions and surface texture parameters. Repeatability, non-linearity, straightness, noise, probe deformation error, numerical error, system long-term stability and sample uniformity have been included in this evaluation.

NS-TuP29 Surface Structure of Metal-Organic Framework Revealed by High-Resolution AFM, *P. Cyganik*, *K. Szelagowska-Kunstman, M. Goryl, M. Szymonski*, Jagiellonian University, Poland

Metal-organic frameworks (MOFs) which consist of organic ligands linked together by metal ions belong to a relatively new class of porous materials.[1] Due to their potential applications in storage, separation, and heterogeneous catalysis, MOFs have attracted increasing attention. So far MOF research has been mainly focused on bulk structure of the material prepared in the form of a powder. Only very recently a new, and radically different, approach was undertaken by exploring the possibilities of MOF growth on surfaces in the form of thin films.[2,3] An important issue for further progress in optimizing growth of MOF crystals, and particularly MOF thin films, is control of their surface structure. Therefore, high-resolution imaging of MOF surfaces is of key importance, as has been previously recognized for zeolites which are analogous to MOFs.

The talk focuses on the AFM study of a MOF single crystal surface.[4] By performing analysis both in air and under ultra high vacuum conditions the high-resolution AFM imaging of a MOF surface is demonstrated. The surface structure of a MOF crystal grown directly on the functionalized substrate is revealed and, moreover, this information is further utilized to optimize growth conditions. Finally, our study clearly demonstrates a much higher structural quality of MOF crystals grown on the substrate in comparison to the conventional powder growth method.

References

[1] O. M. Yaghi et al. **2003**, Nature, 423, 705

[2] O. Shekah et al. **2007** *J. Am. Chem. Soc.* **129**, 15118

[3] E. Biemmi et al. **2007** *J. Am. Chem. Soc.* **129**, 8054

[4] K. Szelagowska-Kunstman et al. **2008** *J. Am. Chem. Soc.* **130**, 14446

NS-TuP31 Enhanced Photovoltaic Performance of DSSC using Broccoli -Like TiO_2 Film with Surface Modification by Zinc Acetate Solution, ***G. Cai****, Y. Chen, C. Huang, J. Liang*, National Dong Hwa University, Taiwan

The broccoli-like TiO_2 film as working electrode for dye-sensitized solar cell (DSSC) was fabricated successfully by flat-flame chemical vapor deposition (FF-CVD) method we developed. The cell efficiency approaches 4.2% with the film thickness about 9~ 13 mm if the film was used without further surface modification. As we known, one source of the energy loss in DSSC is charge recombination occurring between electrolyte and working electrode. In order to reduce charge recombination, we supply a thin metal oxide coating on TiO_2 electrode by using surface modification with metal-containing salt solution as precursor. A higher band gap of the metal oxide semiconductor provides energy barrier to prevent electron transfer back to the oxidative species, and then reduce the charge recombination. However, although thicker metal oxide coating may reduces the rate of charge recombination, it may also reduce the rate of electron injection into the conduction band of TiO_2 working electrode and reduce the cell efficiency. Therefore, the thickness of the metal oxide coating needs to be optimized for the DSSC efficiency enhancement. In this research, we choose ZnO as coating oxide, since ZnO has slightly higher band gap (3.37eV) than TiO_2 (3.2eV). We vary the concentration of zinc acetate solution from 0.1 M to 0.001 M for coating different thicknesses of zinc oxide on TiO_2 working electrode. The crystalline quality and morphologies of surface modified TiO_2 electrodes were characterized by using XRD and FESEM. EDS and XPS were used to confirm the presence of zinc on the surface of TiO_2 electrode. The coating thicknesses were determined by high resolution transmission electron microscopy (HRTEM). The DSSCs using these working electrodes were measured under AM 1.5G 100 mW/cm^2 by Keithley 2400 sourcemeter. As a result, as the concentration of zinc oxide precursor solution decreases from 0.1 M to 0.001 M, the cell efficiency increases from 1.9% to 5.6%. The short circuit current density ( ) increases from 3.59 mA/cm^2 to 11.89 mA/cm^2 as the concentration decreases from 0.1 M to 0.001 M . Furthermore, we also found that the excess thickness of zinc oxide coating will block the electron injection, and results in lower efficiency after surface modification. The drop of efficiency from 4.2% to 1.9% is mainly attributed to the decrease of from 10.08 mA/cm^2 to 3.59 mA/cm^2. It reveals that appropriate thin zinc oxide coating is necessary in reducing charge recombination, while maintaining the high rate of electron injection to the conduction band of TiO_2 working electrode.

NS-TuP32 Thickness Dependence of Thin Film Samaria Doped Ceria Oxygen Sensor, ***M. Nandasiri****,* Pacific Northwest National Laboratory*, R. Sanghavi,* Arizona State University*, S.V.N.T. Kuchibhatla, P. Nachimuthu, M.H. Engelhard, V. Shutthanandan, W. Jiang, S. Thevuthasan,* Pacific Northwest National Laboratory*, S. Prasad,* Arizona State University*, A. Kayani*, Western Michigan University

Resistive oxygen gas sensors stand out among various types of sensors due to their simplicity, low cost, portability, measurement circuit simplification, and low power consumption. Rare earth materials such as pure and doped ceria are potential candidates for resistive oxygen gas sensors due to their unique ability to lose or gain oxygen in response to ambient oxygen concentration. We have recently observed that 6 atom % Sm doping is optimum for obtaining better conductivity using samaria doped ceria (SDC) films. In order to develop oxygen gas sensors based on SDC thin films, it is important to understand the influence of film thickness on the electrical properties. In order to achieve this goal, we have grown SDC thin films on sapphire, Al2O3 (0001) substrates by using oxygen plasma-assisted molecular beam epitaxy. The 6 atom% Sm doped SDC films with thickness ranging from 50 – 300nm have been grown and their conductivity was studied. The resistance of these films, obtained by two probe measurement capability under various oxygen pressures (1mTorr-100Torr) and temperatures (473K to 973K) at a fixed voltage of 2V, will be discussed. The differences in the electrical properties, thereby the oxygen ion conductivity, will be explained based on the chemical and structural characteristics of various films. Structural and chemical characteristics of the as grown films were analyzed by various *in situ* and *ex situ,* surface and bulk sensitive techniques.

In this study we observed that, overall conductivity increases with the film thickness at each temperature and oxygen pressure value. We also observed saturation in the conductivity at film thicknesses above 200nm. With the increasing interest for miniaturized oxygen sensors for high temperature uses, the nano-scale thin film doped ceria sensors may have a significant role to play in various future functional applications. In that sense it is vital to undertake fundamentals studies such as this.

Plasma Science and Technology
Room: Hall 3 - Session PS-TuP

Plasma Science and Technology Poster Session

PS-TuP1 Extension of Aluminum Etch using a Carbon Mask for High Aspect Ratio 70nm Al Etch with a Chlorine Based Chemistry, ***G. Ding****, B. Schwarz, C. Lee*, Applied Materials, Inc

A strippable amorphous carbon hardmask has many advantages over traditional resist or oxide hard masks, it is widely used in frond end applications. However carbon masks for Al etch in backend applications has not been employed. The final CD as well as the aspect ratio that can be achieved with a carbon based mask for Al etching, and how that mask would benefit over traditional PR masks and oxide hard mask are discussed. In this study, we focused on non-fluorine or low-fluorine containing chemistries to achieve a high mean wafers between clean (MWBC) performance. The selectivity/budge for the film stacks (PR => SiON => carbon film =>Al etching) using this approach are illustrated. The carbon mask has shown to achieve less than half of final CD while doubling the mask selectivity over than those best achieved in the PR mask. CD uniformity of **5** nm (3sigma) uniformity was achieved. We demonstrate a wide range of CD tunability (± 20 nm). Throughput and throughput optimization is discussed. The different passivation mechanisms for different masks, PR mask, Oxide hard mask and carbon mask in Al etch are discussed. We demonstrated similar trends between resist and carbon and baseline what leads to excellent transferability of the etch process. This study shows the significant process benefit of the carbon-Al etch in comparison to the oxide HM and PR mask, which will allow Aluminum etch to be continued from an etch perspective to sub 50nm lines with 6:1 aspect ratio.

PS-TuP2 A Study on the Etching Characteristics of Magnetic Tunnel Junction Films for Spin Transfer Torque MRAM, ***M.S. Lee***, KAIST, Republic of Korea*, J.Y. Moon, S.H. Cho, J.K. Jung, S.K. Lee, H.S. Kim, S.K. Park,* Hynix Semicon., Republic of Korea*, W.J. Lee*, KAIST, Republic of Korea

As one of the candidates for universal memory, spin transfer torque MRAM (STT-MRAM) based on magnetic tunnel junction (MTJ) shows several important features such as nonvolatility in data storage and fast writing speed (2~4ns). The most critical engineering challenge for the fabrication of STT-MRAM is the development of etching technology. The etching of magnetic films has severe problems due to the nonvolatility of the metallic byproducts at practical processing temperature. The chlorides, fluorides, bromides and iodides of transition metals have much higher boiling temperatures compared to those of the typical materials used in semiconductor industry. In addition to this intrinsic problem, we should make the MTJ etching profile more vertical while minimizing the redeposition in order to avoid electrical shorting between free layer and pined layer in MTJ structure.

The object of this study is to provide characteristics of dry etching process available for sub 100nm STT-MRAM application. In this study, we investigate the effect of noncorrosive gas chemistry on MTJ etch rate, profile angle and hard mask selectivity, as a function of various process parameters such as RF power, working pressure, gas flow rate and ESC temperature in ICP etching system. It is also examined how the post etching treatment including oxygen plasma ashing and wet cleaning process affects the interface of MTJ films. The characteristics of MTJ interface are carefully analyzed by using high resolution transmission electron microscope (HR-TEM), electron energy-loss spectroscopy in the TEM (TEM-EELS) and X-ray photoelectron spectroscopy (XPS). Highly anisotropic profile of nearly 80 degrees is obtained by optimizing the etching condition and hard mask process scheme. Electromagnetic characteristics are also reported as a function of various etching conditions.

PS-TuP3 Interactions of Plasma with Dielectrics during Ultra Low-k Dual Damascene Etch, ***Y. Zhou**, R. Patz, A. Darlak, K. Zhou, J. Pender,* Applied Materials, Inc., *C. Labelle,* GLOBALFOUNDRIES*, D. Horak*, IBM Research

Higher porosity and new film chemistries are required to drive down the k value of porous ultra low k dielectrics integrated in advanced BEOL stacks. In the k=2.2 porous SiCOH films used in 32nm and 22nm BEOL stacks, higher carbon content and higher Si-C/Si-O ratio render these films more chemically similar to photoresist and to SiCN barrier layers. Hence, there is greatly reduced selectivity between the mask and low-k dielectric, and between the low-k dielectric and the barrier film. The via etch process has to move to a drastically different plasma regime in order to achieve mask selectivity and barrier selectivity, as well as to control RIE lag. New film chemistry and increased porosity also result in new film/plasma interactions, such as surface roughness phenomena 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 modification point. In this work, film surface roughness phenomena will be examined for a k=2.2 porous SiCOH film utilizing a via first trench last integration scheme. Experiments show that surface roughness can arise from several etch steps if plasma conditions are not carefully controlled. Results will be presented with some of the process regimes explored.

This work was performed by the Research Alliance Teams at various IBM Research and Development Facilities.

PS-TuP4 Highly Selective Etching of Silicon Nitride to CVD a-C in Dual-Frequency Capacitively Coupled CH_2F_2/H_2 Plasmas, *J.S. Kim, **N.-E. Lee***, Sungkyunkwan University, Korea

For the fabrication of a multilevel resist (MLR) based on amorphous carbon (a-C) layer and Si_3N_4 hard-mask layer (underlayer), etch selectivity of the Si_3N_4/a-C layer becomes increasingly critical with the feature size reduction. In this work, therefore, the highly selective etching process of the Si_3N_4 layer using chemical-vapor-deposited (CVD) a-C etch-mask was investigated by varying the following process parameters in $CH_2F_2/H_2/Ar$ plasmas: etch gas flow ratio, high-frequency source power (P_{HF}) and low-frequency source power (P_{LF}) in a dual-frequency superimposed capacitively coupled plasma etcher. It was found that infinitely high etch selectivities of the Si_3N_4 layers to the CVD a-C on both the blanket and patterned wafers could be obtained for certain process conditions. In particular, the etch gas flow ratio was found to play a critical role in determining the process window for infinite Si_3N_4/CVD a-C etch selectivity, due to the change in the degree of polymerization. The etch results of patterned ArF PR/BARC(bottom anti-reflective coating)/SiO_x/CVD a-C/Si_3N_4 MLR structure supported the possibility of using a infinitely high selective etch processes of the Si_3N_4 layer using a very thin CVD a-C etch-mask for reduced overall aspect ratio of MLR structure during patterning.

PS-TuP5 Infinitely High Selective Etching of ITO Binary Mask Structure for Extreme Ultraviolet Lithography (EUVL), *Y.R. Park, **N.-E. Lee***, Sungkyunkwan University, Korea

Currently, extreme ultraviolet lithography (EUVL) is being investigated for next generation lithography. Among the core extreme ultraviolet lithography (EUVL) technologies, mask fabrication for EUVL is of considerable importance due to the use of new reflective optics having a completely different configuration compared to those of conventional photolithography. This study investigated the etching properties of EUVL binary mask structure including newly proposed absorber layer of ITO, Ru (capping/etch-stop layer), and Mo-Si multilayer (reflective layer) by varying the gas flow ratio, dc self-bias voltage (V_{dc}) and etch time in Cl_2/Ar inductively coupled plasmas. ITO absorber layer needs to be etched with no loss of Ru layer on the Mo-Si multilayer for fabrication of the EUVL ITO binary mask structure proposed here. The ITO layer could be etched with an infinitely high etch selectivity over Ru etch-stop layer in Cl_2/Ar plasmas with V_{dc} of -50 V even with increasing over etch time. Etching of the stacked mask structures with a 200-nm line/space e-beam resist pattern showed a vertical profile and an etch-stop on the Ru etch-stop layer.

PS-TuP6 Improvement of Surface Roughness in SOI Wafer Fabrication using Cl_2-based Neutral Beam Etching, ***TH. Min**, J.K. Yeon, B.J. Park, S.K. Kang, W.S. Lim, G.Y. Yeom*, Sungkyunkwan University, Korea

For the next generation silicon substrates applied to nano-scale semiconductor devices, silicon-on-insulator (SOI) wafer is known to be one of the outstanding candidates because of the advantages such as high speed, high packing density, immunity from latch-up, low power dissipation, high resistance to ionizing radiation, etc.

For the SOI wafer, the surface roughness of SOI wafer is very important because it can change the physical and chemical properties of the top silicon layer of the SOI wafer. Many approaches have been attempted to reduce the surface roughness of the SOI wafer by chemical mechanical polishing, high temperature annealing, wet etching, etc. but these methods are known to have some problems such as long processing time, reliability of exact thickness control, etc.

In this study SOI wafers were etched by a chlorine neutral beam obtained by the low angle forward reflection of an ion beam and the surface roughness of the etched wafers was compared with that of the SOI wafers etched by a chlorine ion beam. The result showed that the surface roughness of the SOI wafer etched by the chlorine neutral beam was significantly improved compared to that etched by the chlorine ion beam. By etching about 150nm silicon of about 300nm-thick top silicon layer of SOI wafer using the chlorine neutral beam, the rms surface roughness lower than 1.5 Å could be obtained with the etch rate of about 750 Å /min while that etched by the chlorine ion beam showed the rms surface roughness higher than 2.5 Å.

The induced defects in the surface area of the SOI wafer by the ion beam and neutral beam were observed by high-resolution-transmission-electron-microscopy(HR-TEM). An atomic force microscopy(AFM) was employed to measure and evaluated the surface roughness of the SOI wafer before and after the etching process, respectively.

ACKNOWLEDGMENT

This work supported by the National Program for Tera-Level Nano devices of the Korea Ministry of Education, Science and Technology (MEST) as a 21st Century Frontier Program.

PS-TuP7 *In-situ* Evaluation of Ashing Plasma Damages on Porous SiOCH Films Due to Ions, Radicals, and Radiation, ***H. Yamamoto**, K. Takeda, M. Sekine, M. Hori,* Nagoya University, Japan*, T. Kaminatsui, K. Yamamoto, H. Hayashi, I. Sakai, T. Ohiwa*, Toshiba Corporation Semiconductor Company, Japan

Low dielectric constant (low-*k*) materials for interlayer dielectric are important for the improvement of ULSI devices performance. 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. The *in-situ* evaluation is crucial for the clarification of damage generation mechanism because the damaged low-*k* films are modified after exposing to atmosphere. This work investigated the mechanism of plasma ashing damage on the porous SiOCH films by *in-situ* evaluation. We examined the effect of ions, radicals, and radiation using PAPE technique. The thickness and refractive index of porous SiOCH films were measured using *in-situ* spectroscopic ellipsometry. $Si\text{-}CH_3$ bond absorption was measured using *in-situ* FT-IR.

The ashing plasma was exited in a 100 MHz CCP etcher. We adopted porous SiOCH films (k = 2.3) as low-*k* films in this study. The ashing process condition was total gas pressure of 2.0 Pa, 100 MHz source power of 450 W, substrate temperature of 20 °C. In the evaluation, a Si plate or a MgF_2 window which transmits the radiation (greater than 115 nm in wavelength) were placed at 1 mm above or just on the low-*k* film during the ashing. We carried out 4 kinds of experiments : (a) nothing for evaluating of the interaction of ions, radicals, and radiation, (b) Si plate for evaluating of the effect of radicals, (c) MgF_2 window for the interaction of VUV radiation with radicals, (d) MgF_2 window with no space for the effect of VUV radiation.

In the case of H_2 plasma ashing, we confirmed that the interaction of ions, radicals, and radiation or that of radicals and radiation decreased the thickness of the porous SiOCH film. The interaction of radicals and radiation caused the increase of the refractive index. The interaction of ions, radicals, and radiation or that of radicals and radiation caused the decrease of $Si\text{-}CH_3$ bond absorption.

The experimental results showed that H radicals extracted $Si\text{-}CH_3$ bond and that effect was drastically promoted by radiation and ions. The decrease of $Si\text{-}CH_3$ bond caused the decrease of polarizability and density of the film. However, ions made the film contract. Then, the refractive index of the films exposed to ions, radicals and radiation drastically increased. From these results, we proposed a mechanism of the plasma damages on porous SiOCH films.

This work was supported by Grant-in-Aid for Scientific Research (21・10187).

PS-TuP9 Origin of Electrical Changes Occurring at Plasma Etching Endpoints, ***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 impedance magnitude, phase, and dc self-bias voltage. Consequently, these electrical signals are useful for endpoint detection, i.e., for determining when to stop an etch. However, the mechanisms responsible for the observed electrical changes are not well understood. To investigate these mechanisms, we performed experiments and numerical modeling of CF4/Ar plasma etches of thermal silicon dioxide films on silicon substrates, in an rf-biased, inductively coupled plasma reactor. A wave cutoff probe was used to measure the plasma electron density as a function of time during etching. As the etch breaks through the oxide and exposes the underlying silicon, changes in the gas-phase densities of etch products and reactants cause the electron density to increase. This increase (and an accompanying increase in ion current) has a large effect on the measured electrical signals. Using a numerical model and measurements made at varying bias frequencies, the effect of changes in electron density can be distinguished from smaller effects caused by other parameters that may vary at endpoint, including the electron temperature, average ion mass, and the ion-induced emission of electrons from the wafer surface. In addition to explaining the experimental results, the model provides predictions, over a wide range of conditions, for the sensitivity and reliability of the electrical endpoint signals.

PS-TuP10 Optimization of Precursor Injection in an Atmospheric Pressure Plasma Jet System, ***F.J.J. Peeters***, Eindhoven University of Technology, The Netherlands, *R. Dams, R. Rego, M. Dubreuil, D. Vangeneugden,* Flemish Institute for Technological Research (VITO), Belgium, *M. Creatore, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

Atmospheric Pressure Plasma Enhanced Chemical Vapor Deposition (AP PECVD) of thin films is a recently emerged technology, showing important advantages in comparison with the traditional and well established low pressure plasma enhanced deposition methods. The main benefit of AP-PECVD is the potential of cost efficient in-line production without expensive and bulky vacuum equipment.

In this work, an innovative AP plasma jet system is investigated which serves as a pilot system for industrial scale equipment, the VITO PlasmaLine®. Applications include moisture/oxygen diffusion barriers as well as grease barriers, UV curing of coatings or chemical activation of a surface. For industrial application a high throughput (~ 100-1000 m/min) is critical in order to compete with conventional techniques, such as wet chemical coating. Barrier coating deposition by AP-PECVD on polymer substrates has been demonstrated to be superior to wet chemical coating, with less consumption of precursor material [1], though many technical challenges remain to obtain the desired (dynamic) growth rates.

The pilot equipment utilizes a 0.5 mm double slit configuration with 1000-2000 W power input at a frequency of 40-50 kHz with N_2 as the primary carrier gas. By utilizing the plasma afterglow remote from the source, uniform surface treatment can be achieved despite the filamentary discharge in the slits. Deposition on the electrodes is prevented by injection of precursor into the jet and because of the remote nature of the plasma source the thermal load on the substrate is minimized, making it ideally suited for treatment of polymers and paper.

A key area for improvement and upscaling of the pilot system for industrial application is optimization of gaseous and liquid (aerosol) precursor injection. To this end, extensive characterization of the plasma jet is undertaken, including current-voltage, fast imaging and optical emission and absorption measurements, with focus on the dynamics of gaseous and aerosol precursor particles in the jet. For optimum control over the gas distribution and precursor injection, Computational Fluid Dynamic models are presented in conjunction with the experimental work.

[1] Aerosol-assisted plasma deposition of barrier coatings using organic-inorganic sol-gel precursor systems, Vangeneugden D, Paulussen S, Goossens O, et al., CHEMICAL VAPOR DEPOSITION Volume: 11 Issue: 11-12 Pages: 491-496 Published: DEC 2005

PS-TuP11 Plasma Etching of SiO_2 Using a Pin-To-Plate Dielectric Barrier Discharge in Atmospheric Pressure, ***J.S. Oh***, *J.B. Park, E.L. Gil, G.Y. Yeom*, Sungkyunkwan University, Republic of Korea

These days, atmospheric pressure plasmas are being investigated as the application to the flat panel display device processing such as indium tin oxide etching, the deposition and etching of thin film transistor materials (SiO_2, amorphous silicon, and Si_3N_4) in addition to the surface treatment. Especially, among the various atmospheric pressure plasmas sources, much attention has been paid to Dielectric Barrier Discharge (DBD) due to its potential to numerous industrial applications such as plasma ashing, etching, thin film deposition, etc. The DBD, which is consisted of two parallel electrodes covered by dielectric plates, has been studied most widely due to the easier generation of stable glow discharges and the possibility of large-area plasma processing compared with other atmospheric pressure plasma sources.

In this study, using a modified DBD called "pin-to-plate DBD", SiO_2 was etched and its plasma characteristics were investigated. Especially, the effect of additive gas such as CF_4 and C_4F_8 gas to the gas mixture of N_2 (60 slm)/ NF_3 (600 sccm) on the SiO_2 etch characteristics was investigated. The results showed that the increase of C_4F_8 (200 ~ 800 sccm) to the gas mixture decreased the SiO_2 etch rate continuously, while, the addition and increase of CF_4 (1 ~ 10 slm) to the gas mixture increased the SiO_2 etch rate until 7 slm of CF_4 was added and the further increase of CF_4 decreased the SiO_2 etch rate . The increase of SiO_2 etch rate up to 7 slm CF_4 is from the effective removal of Si in SiO_2 by F atom through the removal of oxygen in SiO_2 by carbon in CF_X in the plasma. However, the decrease of SiO_2 etch rate with further increase of CF_4 was related to the formation of a thick C-F polymer layer formed on the SiO_2 surface. The SiO_2 etch rate of about 243 nm/min could be obtained with the gas mixture of N_2 (60 slm)/ NF_3 (600 sccm)/ CF_4 (7 slm) when input voltage and operating frequency to the source were 10 kV and 30 kHz, respectively.

PS-TuP12 Diagnostic Study of Microplasmas in Contact with Saline Solution, *H.W. Chang*, ***A.H. Hsieh***, *C.L. Chen, C.C. Hsu*, National Taiwan University, Taiwan

Microplasmas in contact with saline solution are studied. This microplasma is sustained using a DC power source with the output voltage up to 600 V and the current up to 1.5 A. The powered electrode is the electrode at which the plasma forms. It consists of a thin platinum wire (0.5 mm in diameter) covered by a glass tube except the 2-mm near-tip area. The grounding electrode is a 1 cm * 3 cm- and 0.5-mm-thick stainless steel sheet plate. Both electrodes are immersed in saline solution of various concentrations. The powered electrode serves either as the anode or the cathode, depending upon the operating condition chosen. Diagnostic tools used in this work include a voltage probe and a current probe to monitor the voltage and the current waveforms at the electrode, respectively; an optical emission spectrometer was used to monitor the time-averaged emission spectra. It is shown that the microplasma in 1 M saline solution can be ignited without difficulty for the voltages above 300 V. The forming and sustaining of the microplasma have been found to be a complicated phenomenon associated with the bubble formation and the plasma ignition in the bubbles. As the powered electrode is positively powered (i.e. the anode), two discharge modes, high and low current modes, have been identified. In the low current mode, the microplasma appears to be more stable, and the bubble stays and attaches at the tip of the powered electrode steadily for many seconds, while in the high current mode, the bubbles continuously forms and detaches from the electrode. The major optical emission lines in the high current mode are Na (589 nm) and H (656 nm) emissions. In this presentation, the potential use of this microplasma for materials processing will be discussed.

PS-TuP13 Synthesis of Niobium Oxide Nanowires Using an Atmospheric Pressure Plasma Jet, ***Y. Lin***, *C.C. Hsu*, National Taiwan University, Taiwan

The fabrication of niobium oxide nanowires using an atmospheric pressure plasma was performed. An arc plasma jet sustained by a pulsed power supply with the repetitive power frequency of 25 kHz was used. The O_2 plasma jet was used to treat the 0.025 mm-thick unannealed niobium foils to fabricate niobium oxide nanowires. It was found in this work that the distance between the foil and the jet appears to be the most critical operating parameter for nanowire fabrication. Niobium oxide nanowires with different morphologies were fabricated with oxygen plasma jets at an applied voltage of 300 V and a flow rate of 45 slm, with the foil located at 0.3 ~ 0.7 cm downstream of the plasma jet. Depending upon the distance between the foil and the jet, as well as the operating conditions, the nanowire diameter ranges from 100 to 500 nm, with the length being up to 6 μm. Current work shows that the nanowire diameter increases over time under plasma treatment. Energy-dispersive spectroscopy reveals that the stoichiometry of the fabricated nanowires have the composition ranges from NbO to NbO_3, depending upon the conditions. In this presentation, the correlation between the plasma characteristics and the nanowire structure and its composition will be discussed.

PS-TuP14 Study of an Atmospheric Pressure, Pulsed Arc Plasma Jet: Downstream Characterization and its Application to Thin Film Deposition, ***Y.W. Hsu***, *Y.J. Yang, C.C. Hsu*, National Taiwan University, Taiwan

An arc plasma jet operated under atmospheric pressure was studied. This plasma jet is able to generate a stable plasma using a DC pulsed power source of 20 kHz ~ 40 kHz using nitrogen, oxygen, and clean dry air. In this presentation, diagnostic studies of the plasma jet downstream and the use of this jet for metal oxide fabrication will be presented. The plasma jet downstream was characterized using multiple diagnostic tools. The electrochemical sensor was used to quantify the downstream NO/NO_2 concentration. Multiple thermocouples were used to directly measure the jet temperature and the optical emission of the jet was monitored by an optical emission spectrometer. Spatial-resolved measurements were performed using the above-mentioned diagnostic tools. The downstream species measurements show that the NO density increased from 5 to 116 ppm and the NO_2 decreased from 93 to 52 ppm at 5 cm downstream of the nitrogen plasma jet when the applied voltage increased from 150 V to 350 V under a constant gas flow rate of 45 slm. Jet downstream temperature measurements show that at 1.5 cm downstream of the jet the temperature is approximately 100 °C with 250 V applied voltage and 45 slm. This plasma jet was used for ZnO thin-film deposition. Different precursor injection systems, including a bubbler and an ultrasonic atomizer, were tested. It is shown that the ZnO thin film can be deposited on the glass substrate as confirmed by X-ray photoelectron spectroscopy. The deposition rate and the film quality can be optimized by varying the operating parameters. The correlation between the plasma characteristics and deposited thin film properties will be discussed.

PS-TuP15 Amorphous Silicon Etching Using Atmospheric-Pressure Dielectric Barrier Discharge (APDBD) Plasma, ***H.C. Kwon***, *G.H. Kim*, Seoul National University, Korea, *S.H. Lee*, Korea Institute of Materials Science, Korea, *T.H. Noh*, National Fusion Research Institute, Korea, *S.I. Choi, S.G. Kim, S.K. Lim*, Samsung Electronics Co. Ltd, Korea

Since the process area has been enlarged for increasing the fabrication rate of TFT-LCD, the atmospheric process has been attractively considered. Among the atmospheric processes, the etching is the most challengeable due to the difficulty of etch pattern control and charge damage. Here the etch properties of atmospheric-pressure dielectric barrier discharge (APDBD) has been investigated for the system size of 300 mm × 80 mm. The etching process has been accomplished at 2~3 mm below a blower type APDBD which is a closed system consisted of the top and bottom dielectric electrodes to generate the DBD plasma. Thus, the introduced etchants (SF_6) with carrier gas (N_2) are discharged in the DBD source chamber and the radicals are extruded through the hole of DBD source into the target of amorphous silicon (a-Si) on the patterned silicon nitride (SiNx) with photoresist (PR). The target is set on the moving stage with maximum speed of 100 mm/s. Thus the charge damage may not be considered in this etching system. The etch profiles were exampled with AFM, SEM and others. Result shows the availability of a few micron patterns and etch rate of 600 Å/min with the uniformity below 10% over the substrate. The etch rate and uniformity are sensitive to gas flow rate, the gas mixing ratio, the substrate temperature and the substrate motion. The electrical and optical methods were employed to monitor the discharge properties as the plasma density and gas temperature in source chamber, respectively. Tentatively, it concluded that the ATM process has the property in between the wet and dry (vacuum) process due to its highly collisional condition. The radical generation and transport in the system play a key role in improve the etching, which will be presented.

PS-TuP16 Poly(ethylene glycol) Films Deposited by Atmospheric Pressure Plasma Liquid Deposition and Atmospheric Pressure Plasma-Enhanced Chemical Vapour Deposition : Synthesis of Non-Fouling Surfaces, ***B. Nisol***, Université Libre de Bruxelles, Belgium, *C. Poleunis, P. Bertrand,* Université Catholique de Louvain, Belgium, *F. Reniers*, Université Libre de Bruxelles, Belgium

The role of protein-repelling coatings is to limit the interaction between a device and its physiological environment, by inhibiting the non-specific protein attachment. Plasma-polymerized-PEG (*pp*-PEG) surfaces are of great interest since they are known to avoid protein adsorption [1]. In this study, *pp*-PEG films have been deposited on gold and polyvinylfluoride (PVF) surfaces, by means of atmospheric pressure plasma liquid deposition (APPLD) and atmospheric pressure plasma enhanced chemical vapour deposition (APPECVD) processes. A comparison between those two methods has been made by investigating the chemical composition of the films using infrared reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS) and secondary ions mass spectroscopy (SIMS). By observing the C1s high resolution XPS spectra of our samples, it appears that for APPECVD samples, the hydrocarbon component (285 eV) is increasing as the power of the plasma is increased, revealing a higher fragmentation of the precursor (tetra(ethylene glycol)dimethylether), while for APPLD samples no changes occur. The same conclusion could be made by observing the typical ToF-SIMS peaks (m/z = 45 ($CH_3\text{-}O\text{-}CH_2^+$ and $^+CH_2CH_2\text{-}OH$), 59 ($CH_3\text{-}O\text{-}CH_2\text{-}CH_2^+$), 103 ($CH_3\text{-}(O\text{-}CH_2\text{-}CH_2)_2^+$)) that are decreasing in the case of high powered APPECVD treatments. The non-fouling properties of our samples have been studied with Bovine Serum Albumin (BSA) adsorption. On that purpose, XPS was used to track the presence of BSA on the surface by using the N1s signal coming out from the protein. For the APPECVD samples, a low plasma power (30 W) leads to an important reduction of BSA adsorption (over 90% reduction). However, higher-powered treatments tend to reduce the non-fouling ability of the surfaces (around 50% of protein adsorption reduction for a 80 W deposition). The same order of magnitude of BSA adsorption reduction (over 90%) is obtained for the APPLD surfaces, whatever is the power of the treatment. Those results show an important difference between APPECVD and APPLD processes in terms of power of the plasma treatment.

[1] B.D. Ratner in : R. D'Agostino et al. (eds.), *Plasma Processing of Polymers*, Kluwer Academics Publishers, 1997, pp. 453-464

PS-TuP17 High Refractive Index Polymeric Optical Coatings by Plasma Polymerization, ***L.D. Hyde***, *H.J. Griesser*, Ian Wark Research Institute, Australia

The technique of plasma polymerization has attracted much interest for its ability to deposit uniform polymeric coatings whose thickness can be controlled with nanometer precision via the plasma duration. Thus, plasma polymer (PP) films are well suited to application in optical precision instruments and other devices where high quality optical films are required. However, the range of refractive indices (RI) reported for plasma polymers is quite narrow. One objective of our research is to study how higher RI values can be achieved. Another objective is to develop PP coatings whose RI varies gradually, from a value matching the substrate to a higher value. Gradient Refractive Index (GRIN) films have been produced by plasma polymerization, with the RI changing linearly with the film composition [1]. Here we report on the plasma polymerization of bromoethane and other brominated monomers to create a database of RI versus PP composition prior to using such data for producing GRIN PP films. Factors affecting the PP film composition and thus the RI are plasma deposition power, pressure, deposition rate, and the monomers themselves. Characterization of compositionally homogeneous PP films is performed by optical techniques such as ellipsometry and the data obtained can be extrapolated to provide information about graded polymer films. This is also the case when analyzing homogenous polymer films with techniques such as x-ray photoelectron spectroscopy and Time of Flight Secondary Ion Mass Spectrometry (TOF-SIMS). However, several complementary techniques must be employed when analyzing GRIN films. Techniques such as Small Angle X-ray Scattering (SAXS) and X-ray Reflectometry (XRR) have been utilized because the power of x-rays allows the RI in any medium to be assumed to be unity, as opposed to other optical techniques that essentially deal with optical interfaces and assume samples to be optically homogenous. SAXS is particularly useful as it is capable of measuring polymer blends. Similarly, neutron techniques such as neutron reflectometry (NR) and Small Angle Neutron Scattering (SANS) are complementary to x-ray techniques, as shown by previous work where PP films were analyzed using both XRR and NR [2]. Studies are currently underway to examine the composition of homogenous PP films. One interesting method for depth profiling thin polymer films is TOF-SIMS analysis with a C_{60} gun, which has been used to characterize discrete multilayer structures [3].

[1]Jiang H; *et al*. *Chem. Mater*. **2004**, 16, 1292

[2]Nelson A; *et al*. *Langmuir* **2006**, 22, 453

[3]Zheng LL; *et al*. *Anal. Chem.* **2008**, 80, 7363

PS-TuP18 HfSiON Growth from Hf Metal/SiO_2/Si(100) Stack with Nitrogen VHF-ICP Exposure, ***R. Kage***, *T. Kitajima, T. Nakano,* National Defense Academy, Japan, *T. Makabe*, Keio University, Japan

In the paper, we show the new fablication scheme of high-k dielectric thin film for MOSFETs with fewer process steps, lower impurity, and minimised EOT (equivalent oxide thickness). In the process, high density hafnium metal nano particle with 4 nm diameter is formed on SiO_2/Si surface and subsequent nitrogen plasma exposure (~10 min.) leads to the growth of HfSiON high-k dielectric film with SiN interfacial layer.

Current ULSI technology requires the use of hafnium related high-k dielectrics with ~3 nm thick for MOSFET to lower

the power consumption. HfSiON is the most applicable chemistry for the high-k material with proper energy band

alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO_2 utilizing the thermal interfacial reaction was previously proposed [1]. The process demonstrates remarkably low inpurity in the film due to the lack of carbon in contrast to the case of MOCVD processes. In our case, 2.5 nm thick Hf metal layer is deposited with e-beam deposition source on SiO_2/Si(100) surface uniformly. The

morphology obtained with the in-situ non-contact AFM measurement revealed the surface consists of the high density array of Hf nano particles with the size of 4 nm in diameter.

The exposure of atomic nitrogen and ions from the non-equiliblium plasma enables the introduction of N into the film and increases the interfacial reaction rate of Hf and SiO. Within the first 1 min., the Hf nano particles are

oxynitrided with the N atoms from the plasma and the O atoms supplied from the lower interface judging from the XPS

analysis. The following plasma exposure (~10min.) enables the diffusion of Si atoms into the higk-k film from the

underlying SiO layer. The Si content in the film increases with the exposure time and becomes comparable to the Hf content with 35 min. exposure. The XPS spectrum shows the Si incorporated is mostly nitrided in the film. The spectrum also indicates the interfacial SiO layer is nitrided and this leads to the minimized EOT of the high-k stack structure.

[1] H. Watanabe, Appl. Phys. Lett. 85, 449 (2004).

PS-TuP19 Plasma Characterization of an Unbalanced Magnetron Sputter Deposition System*, **K. Pollock**, J. Hiltrop, J. Doyle*, Macalester College

We present a study of the near substrate plasma properties in an unbalanced magnetron deposition system used to deposit hydrogenated amorphous germanium thin films. The system is equipped with external Helmholtz coils that allow control over the near substrate plasma density. Four plasma diagnostic methods are used to characterize the plasma; a cylindrical Langmuir probe, a flat probe with a guard ring, a retarding field analyzer, and optical emission spectroscopy. The complementary nature of the diagnostics results in a robust determination of the plasma density, electron temperature, and plasma potential. The plasma density inferred from the cylindrical and flat probe results are corroborated by the relative ion currents to the retarding field analyzer. The latter also allows determination of the plasma potential, which agrees well with that inferred from the cylindrical probe results. The electron temperature inferred from the cylindrical probe is approximately corroborated by the relative intensity of the argon optical emission lines, but there is also some evidence that the electron energy distributions have a non-Maxwellian part. In our system the near substrate plasma density can be varied by about a factor of 25. Higher plasma densities near the substrate result in a lower electron temperature and a slight negative shift in the plasma potential. Hydrogen-argon mixtures results in large increases in both plasma density and electron temperature compared to argon-only plasmas. Possible reasons for this phenomena are discussed.

PS-TuP20 Deposition Profile of Carbon Films in Submicron Wide Trenches using H-assisted Plasma CVD*, **T. Nomura**, J. Umetsu, Y. Korenaga, H. Matsuzaki,* Kyushu University, Japan*, K. Koga, M. Shiratani,* Kyushu University, and JST, CREST, Japan*, Y. Setsuhara,* Osaka University, and JST, CREST, Japan*, M. Sekine, M. Hori*, Nagoya University, and JST, CREST, Japan

In recent years hard carbon films have attracted much attention due to their high hardness and wear resistance.[1] Deposition profile of hard carbon films in trenches is one of the concerns. We have succeeded in controlling deposition profile of Cu in trenches of 100 nm in width, and have realized sub-conformal, conformal and anisotropic deposition profiles using H-assisted plasma CVD.[2-4] Here we report these three deposition profiles of carbon films obtained using the H-assisted plasma CVD. Experiments were performed using the H-assisted plasma CVD reactor, in which a capacitively-coupled 28 MHz main discharge and an inductive-coupled 13.56 MHz discharge for an H atom source were sustained.[2-4] This reactor provided independent control of dissociation of deposition material and generation of H atoms. Toluene diluted with H_2 and Ar was supplied at flow rates of 80sccm and 10sccm, respectively. The total pressure was 13 Pa. First, we have studied dependence of deposition rates at the bottom and sidewall of trenches on discharge power of the H atom source. The deposition rates tend to decrease with increasing the power, probably because the flux of H atoms, which etch carbon films, on the surfaces increases. Next, we have studied dependence of the deposition rates on kinetic energy of ions impinging on the surfcases. The deposition rate at the bottom increases significantly with increasing the kinetic energy of ions, while that at the sidewall does not. Irradiation of high energy ions modifies carbon films into a hard structure and the etching rate of such hard carbon films is considerably reduced.[1,5] Another important parameter for deposition profile control is identified to be the substrate temperature. By tuning the H atom flux, ion energy, and substrate temperature, we have realized sub-conformal, conformal and anisotropic deposition profiles of carbon films. Film qualities such as atomic compositions, structure will be presented at the conference.

[1] J. Robertson, Materials Sci. and Engineering R, **37** 129-281 (2004).

[2] K. Takenaka, M. Shiratani, M. Takeshita, M. Kita, K. Koga, and Y. Watanabe, Pure Appl. Chem., **77**, 391 (2005).

[3] K. Takenaka, M. Kita, T. Kinoshita, K. Koga, M. Shiratani, and Y. Watanabe, J. Vac. Sci. Technol., **A22**, 1903 (2004).

[4] J. Umetsu, K. Koga, K. Inoue, H. Matzuzaki, K. Takenaka, M. Shiratani, Surf. Coat. Technol., **202**, 5659 (2008).

[5] A. von Keudell, W. Jacob, J. Appl. Phys. , **79** 1092 (1996).

PS-TuP21 Carbon Particle Formation Due to Interaction between Graphite and Helicon Plasmas*, **M. Shiratani**, S. Iwashita, H. Miyata, K. Koga*, Kyushu University, Japan

Formation of dust particles due to plasma-surface interaction has attracted a great deal of attention in many fields because dust particles can cause quality deterioration in semiconductor manufacturing [1, 2] and can contain a large amount of tritium in fusion devices [3], and so on. Therefore, it is important to reveal their formation mechanisms, their transport as well as their accumulation area. Up to now, we have collected carbon dust particles formed due to interaction between graphite target and helicon plasmas using in-situ and ex-situ collection methods [4], and have analyzed them. Here we report experimental results regarding carbon particle formation due to interaction between graphite and helicon plasmas and discuss their formation mechanisms.

Experiments were carried out with a helicon plasma reactor. Hydrogen or deuterium plasmas were generated by applying pulsed rf voltage of 13.56 MHz to a helicon antenna. The ion density and electron temperature obtained in the helicon discharge reactor are $4x10^{10}$-$3x10^{12}$ cm^{-3} and 4.5-11.8 eV, respectively. Dust particles collected in the helicon plasma reactor can be classified into small spherical particles, agglomerates whose primary particles are around 10 nm in size and large irregular particles. There are many small dust particles of 1 nm-1 μm in size. The typical density ratio among them is $2x10^3$: 1: 3. The smaller their size is, the higher their number density is. The size regions of these dust particles are 1-500 nm for small spherical particles, 50-700 nm for agglomerates and 50 nm-6 μm for large irregular particles, respectively. The three kinds of dust particles suggest three formation mechanisms: CVD growth, agglomeration, and peeling from walls. The dust particles of 10 nm in size have the highest probability to be charged positively, whereas those above 30 nm in size are charged negatively [5]. Agglomeration between a negative large agglomerate and a positive small dust particle takes place during the discharging period.

[1] M. Shiratani, M. Kai, K. Koga, and Y. Watanabe, Thin Slid Films, **427**, 1 (2003).

[2] N. Hershkowitz, IEEE TRANSACTIONS ON PLASMA SCIENCE, **26**, 1610 (1998).

[3] J. Winter, Plasma Physics and Controlled Fusion, **40**, 1201 (1998).

[4] K. Koga, S. Iwashita, S. Kiridoshi, M. Shiratani, N. Ashikawa, K. Nishimura, A. Sagara, A. Komori, LHD Experimental Group, Plasma and Fusion Research, in press.

[5] Y. Watanabe, M. Shiratani, H. Kawasaki, S. Singh, T. Fukuzawa, Y. Ueda, and H. Ohkura, Journal of Vacuum Science & Technology, **A14**, 540 (1996).

Advanced Surface Engineering
Room: Hall 3 - Session SE-TuP

Advanced Surface Engineering Poster Session

SE-TuP1 Characterizations of Normal Incidence Polarizing Beam-Splitter Deposited by Glancing Angle Deposition*, **Y.J. Park**, K.M.A. Sobahan, J.J. Kim, C.K. Hwangbo*, Inha University, Republic of Korea

Glancing angle deposition (GLAD) is a sophisticated technique to fabricate engineered nanostructured thin films for next generation nano and micro devices. In this technique, oblique angle deposition and substrate rotation are employed to control the shapes and porosity of the films, caused by a self-shadowing effect and surface diffusion. Recently, the applications of the properties of the GLAD thin films become the basis of a wide array of industrial components including high-speed gas sensors, optical thin films or nanoporous coatings.

In this study, we investigate the optical and structural properties of normal incidence polarizing beam-splitter. It is realized as a combination of quarter-wave plate, Bragg reflector and opposite quarter-wave plate. The zigzag microstructures of the quarter-wave plates as well as the opposite quarter-wave plates and the helical structure of the Bragg reflector are fabricated by electron beam evaporation using GLAD technique and TiO_2 material is used in this purpose. The physical thicknesses of the opposite and quarter-wave plates are calculated using their anisotropy. It is found that the normal incidence polarizing beam-splitter reflects the p-polarized light while transmits the s-polarized light with wavelength lying in the Bragg regime. The structural and surface morphology of this device are also investigated using scanning electron microscope.

SE-TuP2 Modified Glancing Angle Deposition for Making Nanostructured High Porous SiO_2 Thin Films, ***K.M.A. Sobahan**, Y.J. Park, C.K. Hwangbo*, Inha University, Republic of Korea

Glancing angle deposition (GLAD) is a physical evaporation technique widely used to fabricate nanostructured thin-films materials with controllable shapes and porosity, which is achieved by a self-shadowing effect and surface diffusion. By taking advantage of the versatility of the GLAD technique, it is possible to engineer the materials with unique properties for added value in such areas as optical thin films or nanoporous coatings, high-speed gas sensors, and chemical devices. GLAD thin films can also serve as the foundation of many different types of nano and micro devices.

In this communication, we report the nanostructured porous SiO_2 thin films fabricated by modified GLAD technique. The optical properties of the SiO_2 films fabricated in this technique are investigated and as an application, the antireflection coating (AR) for visible wavelength is designed and fabricated. It is seen that the average reflectance of the AR coating is below 0.04%. The microstructures and the surface morphology are also investigated by using a scanning electron microscope (SEM).

SE-TuP3 Microstructure and Corrosion Resistance of Nano-Crystalline ZrTiN Films on AISI 304 Stainless Steel Substrate, ***Y.W. Lin***, Instrument Technology Research Center, Taiwan, *J.H. Huang, G.P. Yu*, National Tsing Hua University, Taiwan

This study investigated the effect of ratio of Zr/(Zr+Ti) on microstructure and corrosion resistance of ZrTiN thin films. ZrTiN thin films were deposited by reactive magnetron sputtering based on our previous optimum coating conditions (substrate temperature, system pressure, nitrogen flow etc.) for TiN and ZrN thin films. The ratios of Zr/(Zr+Ti) were dominating by changing Ti and Zr target power, and found out the optimum composition with desired properties. The ratio of N/Ti/Zr and composition of ZrTiN thin film were analyzed by X-ray Photoelectron Spectroscopy (XPS) and Rutherford Backscattering Spectrometer (RBS). In terms of phase formation, there were two types of coatings were considered, single-phase solid solution of Zr_xTi_yN and interlacing nucleus of TiN or ZrN in the matrix of Zr_xTi_yN. The thickness of ZrTiN films measured by scanning electron microscope (SEM) was greater than 900 nm. The composition depth profiles measured by Auger electron spectrometer (AES) indicated that the compositions in the ZrTiN films were uniform from the film surface to the 304 stainless steel substrate. The crystal structure of the ZrTiN films was determined by X-ray diffraction (XRD) using a M18XHF-SRA diffractometer with Cu K_α radiation. Reflection line of ZrTiN (002) peak is observed between those of TiN (002) peak and ZrN (002) peak, similarly, reflection line of ZrTiN (111) peak is observed between those of TiN(111) peak and ZrN(111) peak, respectively. The corrosion resistance of ZrTiN films on commercial AISI 304 stainless steel has been investigated by electrochemical measurement. The electrolyte, 0.5 M H_2SO_4 containing 0.05 M KSCN, was used for the potentiodynamic polarization. The potentiodynamic scan was conducted from - 800 to 800 mV (SCE) with scan rate ranging from 10 to 600 mV/min. The variation of Zr/(Zr+Ti) ratio on the microstructure and corrosion resistance of ZrTiN film was investigated.

SE-TuP4 Light Out-Coupling Characteristics Based-on the Interfacial Electronic Structure of MoO_x-doped Fullerene, a Potential Hole Ohmic-Contact Layer for Organic Semiconductor, ***J.T. Lim**, J.W. Kwon, G.Y. Yeom*, Sungkyunkwan University, Korea

Recently, the interest on the ohmic contact between the metal-organic interfaces has been actively increasing to inject charge carriers between electrodes and an adjoining organic layers more efficiently. Among those contact, the hole-injecting properties without a barrier height between anode and a hole-injecting layer are very important for driving the devices to a high brightness and a high luminous efficiency in organic semiconductors, such as the organic light-emitting diodes, organic solar cells, and organic thin film transistors. Here, we reported on the new ohmic-hole contact system of MoO_x-doped fullerene. The phosphorescent organic light-emitting diode with fullerene doped with 10% MoO_x showed the maximum brightness of 86500 cd/m^2 and the power efficiency of 15.6 lm/W at a luminance of 100 cd/m^2. The improvement of the light out-coupling property by inserting the MoO_x–doped fullerene layer between anode and a hole-transporting layer is due to the formation of an ohmic contact without the barrier height in a hole injection (Φ_B^h) as well as the raising of the band banding by pinning Fermi levels in the interfaces. The mechanism for the ohmic hole-injecting characteristic from anode to MoO_x–doped fullerene was proved from an ultraviolet photoemission spectroscopy (UPS) sepctra. In UPS spectra, the highest occupied molecular orbital (HOMO) level of the interface formed between two materials nearly approaches to Fermi level of anode.

SE-TuP5 Novel Top-Down Fabrication Technique for Metallic Nanoparticles Using Microsphere Self-Assembly and Oblique Angle Thin Film Deposition, ***M.A. Roddy**, E.M. Kirkpatrick, S.R. Kirkpatrick*, Rose-Hulman Institute of Technology

Metallic nanoparticles are of significant interest to the biomedical, electronics, optical, and magnetic fields. We have worked to develop a novel technique to fabricate nanoparticles on the order of 100 – 1000 nm. The process uses a self-assembled planar array of polystyrene microspheres[1] as a structured template for oblique angle deposition of a thin film, such that the tops of the spheres are covered with 'caps' (see Attachment 1). The spheres provide mutual shadowing from deposition, which determines the nucleation sites for metallization resulting in semi-spherical and hemispherical caps. Nanoparticle caps of both SmCo and chrome were fabricated. Chrome caps were prepared by allowing a mixture of 800 nm microspheres and DI water to dry on a substrate (glass, oxidized silicon, or bare silicon). 100 nm of chrome was then sputtered on the microspheres at angles of 80, 75, and 70 degrees normal to the surface. The sputtering parameters were base pressure of 2E-8 torr, sputter gas pressure of 2E-3 torr, and power of 300 W. In order to characterize the resulting nanoparticles via SEM the polystyrene was removed either by methanol or oxygen plasma ashing. A similar method was used for the SmCo samples, however, both an underlayer and overlayer of 15 nm NiCr was deposited head-on in order to prevent oxidation of the SmCo. Morphology of the samples depended on deposition angle and the deposition direction compared to the orientation of the self-assembled template and the resulting particles ranged in size from 350-700 nm.

SE-TuP6 Tribological Behaviour of TiAlN/TiAlN/Pt Multilayers Deposited on Stainless Steels, ***M. Flores**, J. Garcia, E. Rodriguez,* Universidad de Guadalajara, Mexico, *L. Huerta,* Universidad Nacional Autonoma de México, *E. De las Heras*, Instituto Nacional de Tecnología Industrial, Argentina

In the present work we report the results of studies about the influence of Pt layers on the wear resistance of TiAL/TiALN multilayers deposited on 316L stainless steel by magnetron sputtering using targets of TiAL and Pt. Coating types investigated included TiAlN, TiAlN/TiAL, TiAlN/TiAL/Pt and duplex coatings with substrates nitrided by pulse plasma nitriding. The thickness of the Pt layers was from 50 nm to 200 nm and the period of TiALN/TiAL multilayer from 250 to 500 nm. The friction and wear tests were performed on a ball-on-flat tribometer and conducted in dry (unlubricated) conditions at room temperature. The loads used were from 2N to 10N and the oscillating frequency from 1 Hz to 5 Hz. The structure, composition and thickness of multilayers were studied by means of XRD, RBS and ellipsometry analysis. The surface topography and wore surface were studied by means of optical microscopy and profilometry. The results indicate that coefficient of friction (COF) of TIALN coatings decreased when metal layers are introduced.

SE-TuP7 Physical Processes for Low Temperature Plasma Activated Wafer Bonding, ***T. Plach**, K. Hingerl,* Johannes Kepler University, Austria, *V. Dragoi, G. Mittendorfer, M. Wimplinger*, EV Group, Austria

Low temperature plasma activated direct wafer bonding (LTPADWB) for Si-SiO_2 interfaces is a process that lowers the required annealing temperatures necessary for reaching high bond strength. Bulk strength can be realized by plasma activation with subsequent annealing at 300°C. The mechanism behind this improvement is still under discussion.

At this temperature, half of the bulk strength is reached already with conventional wafer bonding. The low temperature steps for the hydrophilic process are interpreted as follows: Up to 100°C the substrate surfaces are held together via van der Waals interaction which is mediated by a few monolayers of water. In the range of 100-200°C the water diffuses away from the interface both along the interface and through the oxide into the crystalline bulk, where it reacts with the silicon and forms oxide. The remaining half of the bond strength is usually attributed to a closing of gaps at the interface[1], which starts at the softening temperature of the thermal oxide at around 850-900°C.

To clarify the mechanism for this commercially available process, different bonding experiments were performed to evaluate the lifetime of the surface activation and the achievable bond strength when using substrates with various orientations. Interfaces of bonded wafer pairs were investigated by transmission electron microscopy (TEM). TEM images clearly show that there is no discernible interface between the native oxide on one side and the thermal oxide on the other side.

By covering half of the wafer during plasma activation, comparisons between the activated and non-activated region could be made by atomic force microscopy, by spectroscopic ellipsometry, by Auger analysis and by X-ray photoelectron spectroscopy.

It was found that the top surface stoichiometry is chemically changed, which favors bonding. Finally a model for the mechanism that explains the experimental results will be presented.

Keywords: wafer bonding; plasma; low temperature

References

[1] Q.-Y. Tong, U. Gösele, *Semiconductor Wafer Bonding: Science and Technology,* Wiley, (1998)

Surface Science
Room: Hall 3 - Session SS-TuP

Surface Science Poster Session I and Mort Traum Finalists

SS-TuP1 MORTON S. TRAUM AWARD FINALIST: Morphology and Chemical Reactivity of Bi-Metallic Au-Pd Clusters, ***E. Gross****, *M. Asscher*, The Hebrew University of Jerusalem, Israel

Bi-metallic clusters have unique catalytic properties, since one metal can modify the electronic and thus the catalytic properties of the other metal. Here we describe a unique preparation method of bimetallic Pd-Au nano-clusters. The growth mode is based on initial evaporation of metal atoms on top of amorphous solid water adsorbed on SiO_2/Si(100) substrate at 100K under ultra high vacuum (UHV) conditions. The ice buffer layer separates the small metallic seed clusters from the substrate. Subsequent annealing to 300K desorbs the water molecules, resulting in aggregation and growth of nano-clusters in a Buffer Layer Assisted Growth (BLAG) mechanism.

Transmission Electron Microscope (TEM), Energy Dispersive X-ray (EDX) and X-Ray Diffraction (XRD) measurements revealed that by modifying the clusters preparation procedure either segregated or alloyed Pd-Au clusters can be formed. The composition of the different clusters was also verified by optical surface plasmon resonance (SPR) absorption measurements.

Temperature Programmed Reaction (TPR) measurements have shown that adsorption of acetylene on top of Pd-Au alloy clusters has led to efficient conversion to ethylene. Benzene was also formed at an order of magnitude smaller rate. Pd-Au alloy clusters have demonstrated significantly higher reactivity than the monometallic clusters. Increasing the surface defects density by Ar^+ ion sputtering enhanced the thermal stability and sintering resistance properties of the Pd-Au clusters.

SS-TuP2 MORTON S. TRAUM AWARD FINALIST: Direct Observation of Hydrogen-Bond Exchange within a Single Water Dimer, ***T. Kumagai****, *M. Kaizu, H. Okuyama,* Kyoto University, Japan, *S. Hatta, T. Aruga,* Kyoto University, JST-CREST, Japan, *I. Hamada, Y. Morikawa*, Osaka University, Japan

The nature of the hydrogen bond is related to many physical, chemical and biological processes. The structure and dynamics of water dimers, which consist of hydrogen-bond donor and acceptor molecules, have been subjects of extensive research as a prototype of much more complex hydrogen-bonding systems. The water molecules in a free water dimer rearrange the hydrogen bond through quantum tunneling among equivalent structures [1]. Recently, we reported the visualization in real space of hydrogen-bond exchange process governed by quantum tunneling within a single water dimer adsorbed on a metal surface with a low-temperature scanning tunneling microscope (STM) [2].

The experiments were carried out in an ultrahigh vacuum chamber equipped with STM operating at 6 K. The Cu(110) was cleaned by repeated cycles of argon ion sputtering and annealing. The surface was exposed to H_2O or D_2O gases via a tube doser below 20 K. We conducted the experiments at very low coverages, where water molecules exist mainly as isolated monomers and dimers on the surface.

A water dimer is characterized by its bi-stable fluctuating image due to the interchange motion of the hydrogen-bond donor and acceptor molecules. The STM image of the dimer shows dramatic change upon substitution with heavy water. The interchange motion of $(D_2O)_2$ is much slower than that of $(H_2O)_2$. The interchange rate was determined to be $(6.0 \pm 0.6) \times 10\ s^{-1}$ for $(H_2O)_2$ and $1.0 \pm 0.1\ s^{-1}$ for $(D_2O)_2$ by monitoring the interchange events in real time. The large isotope effect (~60) suggests that the rate-limiting process involves quantum tunneling. In addition, DTF calculation revealed that the barrier of the interchange on Cu(110) is 0.24 eV. This cannot be overcome via mere thermal process at 6 K, which corroborates that the interchange proceeds through tunneling.

Furthermore, the interchange rate is enhanced upon excitation of the intermolecular mode that correlates with the reaction coordinate. While the interchange motion is intrinsic at low bias voltage, as indicated by negligible tip effect, it becomes tip assisted at voltages above 40 mV. The threshold voltage is determined to be 45 ± 1 (41 ± 1) mV for H_2O (D_2O) dimers. The barrier for the interchange (0.24 eV), however, much larger than the energy transferred from a tunneling electron (45 mV). Consequently, we propose that the interchange tunneling is assisted by vibrational assisted tunneling process.

[1] R. S. Fellers, C. Leforestier, L. B. Braly, M. G. Brown, and R. J. Saykally, Science 284, 945 (1999).

[2] T. Kumagai *et al*. *Phys. Rev. Lett.* 100, 166101 (2008).

SS-TuP3 MORTON S. TRAUM AWARD FINALIST: A Surface-Chemical Perspective on the Success (and Failure) of Metalorganic Compounds as Precursors for Thin Film Deposition, ***J.C.F. Rodríguez-Reyes****, *A.V. Teplyakov*, University of Delaware

Fundamental studies focused on understanding the key surface processes that introduce contaminants into a growing film are essential for achieving a contaminant-free thin film deposition. In the case of the metal alkylamide precursor $Ti[N(CH_3)_2]_4$, we have obtained experimental evidence of two chemical reactions on a Si(100) surface that explain the uncontrolled incorporation of carbon during deposition, namely a surface attachment through a ligand and a feasible C-H bond scission on the surface. For both reactions, the nitrogen p-orbital in the alkylamide precursor plays a significant role, not only favoring the interaction of a N atom with electron-deficient surface sites, but also weakening anti-periplanar C-H bonds. The realization of the important role that the heteroatom in the ligand plays during surface reactions prompted us to start a comprehensive computational investigation of N-containing and O-containing metalorganic precursors, such as amidinates, guanidinates, alkoxides and acetonates. In addition, we consider metal alkyls and cyclopentadienyl precursors. An effective comparison of the surface reactivity of these compounds and their ability to adsorb and decompose on a surface is achieved by simulating the reactions on a silicon surface cluster model using the same methods. Our results corroborate the model established for the alkylamide precursors, where metalorganic precursors adsorb preferentially through the formation of a N- or O- dative bond to the surface. However, further decomposition mechanisms are less favorable for certain types of precursors, such as amidinates and guanidinates, where the p-orbital of the N atoms is delocalized and therefore does not favor the scission of nearby C-H bonds. Oppositely, alkylamides, alkoxides and acetonates are found to readily decompose on the surface. When heteroatoms are absent (e.g. in the case of cyclopentadienyls) adsorption is a significantly less favorable process and decomposition pathways leading to carbon incorporation are less feasible than for other compounds. This investigation is intended to set a ground work for future investigations devoted to understanding and controlling contamination mechanisms during film deposition.

SS-TuP4 MORTON S. TRAUM AWARD FINALIST: Nanoparticle Growth from Copper Metal-Organic Precursors on H-terminated Silicon Surfaces, ***K.A. Perrine****, *A.V. Teplyakov*, University of Delaware

Scaling down of the features needed for microelectronic industry has been redefined with the advances in atomic layer deposition (ALD) methods. At the same time, chemical vapor deposition (CVD) of copper has been used in interconnect devices in the electronics industry for several decades. For a controlled copper deposition, it is desirable to combine the clean ligand removal from the precursor molecules (such as, Cu^I (hexafluoroacetylacetonato) vinyltrimethylsilane or Cu(hfac)VTMS) with the control of the ALD process.

In this work, copper nanoparticles were grown by CVD on hydrogen-terminated silicon surfaces to minimize interfacial contamination and effectively remove the hfac and VTMS ligands for clean Cu deposition. During the deposition process, the amount of copper deposited at room temperature is limited by the amount of hydrogen available for ligand removal. Both H-terminated Si(111) and Si(100) surfaces exhibit the growth of nanoparticles, as observed by AFM, and the amount of copper deposited depends on the amount of surface hydrogen present, showing

---

* Morton S. Traum Award Finalist

similarity to ALD growth mechanism. Both AFM and SEM confirm copper nucleation. In addition, the growth kinetics of Cu(hfac)VTMS is compared for monohydrogen-terminated Si(100) and hydrogen-terminated Si(100)-3x1 using *in situ* MIR-FTIR. The growth on OH- and NH- terminated surfaces will be compared to that on H-terminated surfaces. *In situ* FTIR spectroscopic studies indicate surface reaction by analysis of the Si-H region and are compared to *in situ* and *ex situ* XPS studies to confirm metallic copper deposition. Silicon surfaces, Si(111) and Si(100), yield different results and indicate that copper growth starts at defect sites. These results set a foundation for growth of clean copper on reducing solid substrates.

SS-TuP5 MORTON S. TRAUM AWARD FINALIST: Room Temperature Molecular-Resolution Characterization of Self-Assembled Organic Monolayers on Epitaxial Graphene, ***Q.H. Wang****, *M.C. Hersam*, Northwestern University

Graphene has attracted significant attention due to its unique electronic structure, high carrier mobilities, and quantum relativistic phenomena. Epitaxial graphene grown on SiC(0001) is a promising material for next-generation technology because it allows for wafer-scale processing. In order to realize its full potential for a diverse range of devices, the bare graphene sheet must be incorporated with other materials via chemical functionalization schemes. Recent progress reported in the literature include the demonstration of atomic layer deposition of Al_2O_3 on mechanically exfoliated graphene sheets functionalized by carboxylate-terminated perylene derivatives,[1] and the formation of monolayers of 3,4,9,10-perylene-tetracarboxylic dianhydride (PTCDA) at cryogenic temperatures on epitaxial graphene.[2] In this study, we report the room-temperature formation of self-assembled monolayers of PTCDA on epitaxial graphene.[3] We characterize the molecular ordering and electronic properties of these monolayers using ultrahigh vacuum (UHV) scanning tunneling microscopy (STM). The molecules self-assemble into stable, well-ordered monolayers that are arranged in a herringbone phase with extended domains spanning hundreds of nanometers. At submonolayer coverage, PTCDA forms stable, isolated molecular islands. The molecular ordering is unperturbed by either defects in the epitaxial graphene or atomic steps in the underlying SiC surface. Scanning tunneling spectroscopy (STS) performed on the PTCDA monolayers reveals strong features in the electronic density of states that are distinct from the pristine graphene regions. The demonstration of robust, uniform organic functionalization of epitaxial graphene presents opportunities for exploring self-assembly chemistry on graphene, tailoring the chemical functionality of graphene, and templated growth and deposition of other materials as potential routes toward realizing graphene-based molecular electronic and sensing devices.

[1] X.R. Wang, S.M. Tabakman, and H.J. Dai, *J. Am. Chem. Soc.* **130**, 8152-8153 (2008).

[2] P. Lauffer, K.V. Emtsev, R. Graupner, T. Seyller, and L. Ley, *Phys. Status Solidi B*, **245**, 2064-2067 (2008).

[3] Q.H. Wang and M.C. Hersam, *Nature Chemistry*, in press (2009).

SS-TuP6 MORTON S. TRAUM AWARD FINALIST: Size-Dependent Catalytic Properties of Pt Nanoparticles Synthesized by Reverse Micelle Encapsulation: Oxidation, Reduction, and Reactivity, ***J. Croy****, *L.K. Ono, S. Mostafa, H. Heinrich, B. Roldan Cuenya*, University of Central Florida

The oxidation of Pt and the reactivity of Pt oxides are of fundamental importance in catalysis, and although much research has been conducted on the interaction of oxygen with Pt surfaces, most of the work is confined to UHV with bulk materials such as Pt(111). In this work we will explore the size-dependent oxidation and reduction properties of Pt nanoparticles (NPs) synthesized by reverse micelle encapsulation. We use in-situ O_2-plasma treatments in conjunction with e-beam heating and X-ray photoelectron spectroscopy (XPS) to monitor the temperature-dependent reduction of $Pt^{\delta+}$ species in NPs with distinct size distributions. In addition temperature programmed desorption (TPD) was conducted to monitor the oxygen phases developed on our NP samples. These results are compared with the same experiments conducted on a Pt(111) crystal. In parallel to UHV studies, the activity of pre-oxidized Pt NPs, supported on nanocrystalline ZrO_2, was tested for methanol (MeOH) decomposition and oxidation reactions at atmospheric pressure using a packed-bed reactor coupled to a quadrupole mass spectrometer (QMS). Transmission electron microscopy (TEM) was conducted for morphological information and XPS was used to characterize samples both before and after interaction with MeOH.

SS-TuP7 A Novel Spectrometer for Wide Angle and High Pressure Photoemission, ***A. Thissen***, *S. Mähl, T. Kampen, O. Schaff*, SPECS GmbH, Germany

New scientific opportunities in key research fields like catalysis, research on liquid and aqueous samples, and living matter demand a combination of in-situ x-ray photoemission experiments (XPS) with high-pressure environments of up to 10 mbar.

To address these exciting new challenges we have developed a novel photoemission spectrometer that enables angle resolved photoelectron spectroscopy (XPS) at pressures up to 10 mbar with an angular acceptance of +/- 22°. This new set-up not only dramatically increases the spectrometer transmission but also allows non-destructive depth profiling exploiting the angular dependence of the XPS signal.

The instrument consists of a differentially pumped PHOIBOS 150 hemispherical analyzer with a pre-lens. This newly developed pre-lens increases the acceptance angle of the PHOIBOS analyzer by a factor of 5. At the same time it allows extremely efficient differential pumping of the gas atmosphere above the sample.

SS-TuP8 In Situ High Pressure X-ray Photoelectron Spectroscopy Studies of the Adsorption of CO and O_2 on Au Nanoparticles Grown on TiO_2(110) Surfaces, ***P. Jiang***, *S. Porsgaard, F. Borondics, M. Kober, Z. Liu, M. Salmeron, H. Bluhm*, Lawrence Berkeley National Laboratory

Gold nanoparticles supported on TiO_2 surfaces are effective catalysts for CO oxidation. Despite numerous studies on this system, the fundamental mechanism is still controversial, partly due to the challenging pressure gap. Using our special in situ high pressure X-ray photoelectron spectroscopy (HP-XPS), we systematically investigated the adsorption of CO and O_2 on Au nanoparticles grown on TiO_2(110) surfaces with different stoichiometries under real reaction conditions. We found that the synergism between Au and TiO_2 surfaces plays the key role for the whole reaction process.

SS-TuP10 DFT Study of Oxygen Vacancy Formation in a Diesel Oxidation Catalyst: Pt/CeO_2(111), ***T.Q. Nguyen***, *M.C.S. Escaño, S. Kunikata, H. Nakanishi, H. Kasai,* Osaka University, Japan, *H. Maekawa, K. Osumi, Y. Tashiro*, Isuzu Advanced Engineering Center, Ltd., Japan

Air pollution from automobile exhaust is one of the major environmental problems in modern civilization. In order to reduce the amount of noxious pollutions, the diesel oxidation catalyst (DOC) systems are widely used. In the DOC system, CO and Hydrocarbon (HC) are oxidized to harmless chemical substances such as H_2O, CO_2, and NO is converted to NO_2.[1-4] DOCs have a honeycomb-like, monolithic structure. The monolith support is made either from metallic (stainless steel) or ceramic material and coated with a so-called "washcoat". The washcoat consists of high porous oxides, such as γ-Al_2O_3 (alumina), and precious metals, such as Pt, Pd, and Rh plus more additives (e.g., CeO_2 and ZrO_2) to increase the catalytic activity or to stabilize the structure of the catalyst. In DOCs, Cerium is present in high quantities in the form of CeO_2. Cerium renders multiple functions, the most vital of which is to store and to release oxygen under fuel-lean and fuel-rich conditions. This is so-called the oxygen storage capacity (OSC), which allows the catalyst to operate over wider air to fuel ratio.[5]

In this work, we investigate the adsorption of Pt atom on unreduced and reduced CeO_2(111) surface by using first-principles method. With the aim of having a better understanding of the catalytic properties of Pt/CeO_2 for further development and improvement of DOCs, we concentrated on the details of Pt adsorption on CeO_2, the formation of oxygen vacancies at Pt/CeO_2 surfaces and how it affects the geometric and electronic structures as well as chemical properties of surface. We found that, some metal induced gap states appeared under the adsorption of Pt, which is due to the strong interaction between Pt 5*d* and O 2*p*. This is the factor that makes the Pt/CeO_2 system more active than the clean CeO_2 surface. In addition, the adsorption of Pt accelerates the formation of surface vacancies and enhances the OSC. A more detailed discussion of these results will be conducted in the meeting.

References

[1] R. J. Farrauto, K. E. Voss, Appl. Catal. B: Environmental 10 (1996) 29

[2] K. M. Adams, J. V. Cavataio, T. Sale, W. A. Rimkus, R. H. Hammerle, SAE 962049 (1996)

[3] W. A. Majewski, J. L. Ambs, K. Bickel, SAE 950374 (1995)

[4] E. Xue, K. Seshan, J. G. Ommen, Appl. Catal. B: Environmental 2 (1993) 183

[5] H. C. Yao, Y. F. Yu. Yao, J. Catal. 86 (1984) 254

---

* Morton S. Traum Award Finalist

SS-TuP11 Surface Electronic Structures and Chemical States of O_2 on Pt_3M [111], (M = Fe,Co,Ni), *Y.-S. Kim,* Lawrence Berkeley National Laboratory and Hanyang University, Korea, ***B.S. Mun**,* Hanyang University, Korea and Lawrence Berkeley National Laboratory, *V. Stamenkovic, N. Markovic,* Argonne National Laboratory, *A. Bostwick, E. Rotenberg, P.N. Ross*, Lawrence Berkeley National Laboratory

With x-ray photoemission spectroscopy (XPS), surface electronic structures and chemical states of O_2 on Pt_3M [111] single crystals are investigated at various surface temperature, T = 30~150K. At T=30K, both physisorbed and chemisorbed oxygen molecules are present on the surfaces. As the surface temperature is increased to 150K, molecular oxygen on the surface undergoes a phase transition from weakly bounded physisorbed states to chemisorbed states, i.e. an atomic oxygen states. From the measurements of Fermi surface with angle-resolved XPS, Pt [111] surface shows a clear signature of charge transfer along M direction upon the adsorption of oxygen molecules. However, all other Pt_3M surfaces exhibit little changes near Fermi surface at various temperatures. The correlation between the electrochemical reactivity and surface electronic structures on Pt_3M will be presented.

SS-TuP13 Improvement of Metal Oxide Catalyst Reactivity by Modification of Surface Fermi Level, ***M.C. Kratzer***, University of Illinois at Urbana-Champaign, *F. Nasim, A.S. Bhatti,* Comsats Institute of Information Technology, Pakistan, *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 metal oxide semiconductors support space charge, it is possible for surface electronic properties to couple to bulk electronic properties. Consequently, electronic "band engineering" can be employed to optimize surface reactivity and affect either thermal catalysis or photocatalysis. For instance, 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. Alternatively, the direction and magnitude of the near-surface electric field within the space charge region can be adjusted by bulk doping which, in turn, affects the flow of photogenerated charge carriers toward the surface in photocatalysis. The present work describes the applicability of photoreflectance (PR), a type of modulation spectroscopy, to understanding semiconductor surface-bulk coupling in the context of catalysis using TiO_2 as an example metal oxide. The approach involves the synthesis of a thin film of the semiconductor on a silicon substrate by chemical vapor deposition or atomic layer deposition. N- and p-type dopants are introduced into TiO_2 during deposition to produce samples of varying doping levels. The physical and chemical properties of the thin films are characterized using ellipsometry, x-ray diffraction, and x-ray photoelectron spectroscopy. Detailed electrical characterization employing a Schottky diode test structure is undertaken to obtain a precise estimate of carrier concentration. PR is then utilized to better understand the effect of film thickness and uniformity, crystal structure, and doping on the position of the surface Fermi level. The results shed light on the properties of the TiO_2 surface as it relates to thermal catalysis and photocatalysis, and enable unprecedented precision in the tailoring of metal oxide catalysts to ensure optimal surface reactivity.

SS-TuP18 Transition of the Molecule Orientation during Adsorption of Terephthalic Acid on Rutile TiO_2, ***A. Nefedov***, Ruhr University of Bochum, Germany, *P. Rahe, M. Nimmrich,* University of Osnabruck, Germany, *M. Naboka,* Ruhr University of Bochum, Germany, *A. Kuehnle,* University of Osnabruck, Germany, *Ch. Woell*, University of Bochum, Germany

Chemically functionalized surfaces play an important role in many nanotechnological applications. However, only few attempts have been made so far to create a chemically functionalized metal oxide surface by adsorption of organic molecules, even though metal oxide surfaces provide anisotropy and specific adsorption sites that lead to well-ordered monolayers. Terephthalic acid (TPA) is a versatile molecular linker and has, consequently, received considerable attention with regard to the assembly of three-dimensional self-assembling porous frameworks stabilized by metal-carboxylate bonds, as well as in two-dimensional supramolecular architectures at surfaces. In particular, TPA/TiO_2 is a promising system to create an overlayer of upright oriented molecules exposing an organic surface terminated by carboxyl groups.

The coverage-dependent adsorption of terephthalic acid on rutile TiO_2 was investigated by means of non-contact atom force microscopy (NC-AFM) and near-edge x-ray absorption fine structure (NEXAFS) spectroscopy [1, 2] under ultra-high vacuum conditions at room temperature. Experiments were performed in two separate systems, one for performing the NC-AFM measurements and the second UHV system using synchrotron radiation for the NEXAFS experiments, which were carried out at the HE-SGM beamline of BESSY II. Individual molecules are observed to adsorb in a flat-lying geometry at low coverages up to ~0.3 monolayer (ML). The molecules are immobile at room temperature, implying a diffusion barrier of larger than 0.8 eV. This rather high value might be explained by an anchoring to surface defect sites. A transition from flat-lying to upright-oriented molecules is revealed by NEXAFS when saturation coverage is achieved. High resolution NC-AFM images reveal two different structures at coverages between ~0.8 ML and 1 ML: (i) a well-ordered (2×1) structure and (ii) a mixed structure of molecular rows oriented along the [001] crystallographic direction. The latter structure might originate from a pairwise interaction of two neighboring molecules through the top carboxyl groups. Further increase of the exposure results in a saturation of the corresponding signal in the NEXAFS spectra revealing that the growth of TPA on TiO_2 at room temperature is self-limiting.

1. S. Reiss, H. Krumm, A. Niklewski, V. Staemmler, Ch. Wöll, J. Chem. Phys. 116, 7704, (2002).

2. D. Käfer, L. Ruppel, G. Witte, Ch. Wöll; Phys. Rev. Lett., 95, 166602 (2005).

SS-TuP19 Effect of Rapid Thermal Annealing on the Electrical and Optical Properties of Reactively Sputtered Ag_2O Thin Films, ***C.C. Tseng***, National Chung Hsing University, Taiwan, *J.H. Hsieh,* Ming Chi University of Technology, Taiwan, *W. Wu*, National Chung Hsing University, Taiwan

Silver oxide films were deposited on glass substrates by magnetron sputtering of a silver target in various Ar–O2 reactive mixtures with deposited temperature. After deposition, some of these films were annealed using a rapid thermal annealing (RTA) system, with the variation of temperature. A UV-VIS-NIR photometer and a Hall measurement system were used to characterize the optical and electrical properties of these films. The films show a systematic changed from Ag2O(hexagonal) phase to Ag+Ag2O(cubic) phases at various annealing temperatures. When the annealing temperature is higher than 300oC, the Ag2O(hexagonal) phase transformed to Ag+Ag2O(cubic) composite phases. Accordingly, the band gap of these films will change, along with the optical and electrical properties.

***Keywords**:* silver oxide, UV-VIS, rapid thermal annealing, optical property, electrical property.

Vacuum Technology
Room: Hall 3 - Session VT-TuP

Vacuum Technology Posters and Student-Built Vacuum Systems Poster Competition

VT-TuP1 New Developments at ISIS – The Worlds Leading Pulsed Neutron and Muon Source, ***S. Patel***, STFC Rutherford Lab, UK

Over the past 12 months there have been major advances at the above research facility operated by STFC, which is based at the Rutherford Appleton Laboratory, Oxford, England. In addition to the Second Target Station (TS2) becoming operational with a suite of seven new instruments, there have also been developments to improve the performance and reliability of existing instruments on Target Station One. Some of the key vacuum challenges faced during the last year will be outlined here, together with details of the challenges that lie ahead.

VT-TuP2 Vacuum Pressure Simulation for the Insertion Device Beamline at X-Ray Ring of NSLS, ***J.-P. Hu***, Brookhaven National Laboratory

Beamline 9 at the X-ray storage ring of the Brookhaven Lab's National Synchrotron Light Source has been upgraded from a conventional bending magnet beamline to an insertion device beamline, with installation of a mini gap undulator (MGU) between the two RF cavities at upstream of dipole magnet. The new water-cooled undulator, which is made of neodymium-iron-boron magnet and vanadium-permandur poles, was tested to generate a high-brightness coherent 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). To meet required ultra-high vacuum (UHV) for beam transport under minimum scattering and aberration, the X-9 front-end was also upgraded, with installation of following provisions: fixed-aperture photon mask for beam filtering, high-density safety shutter for *bremsstrahlung* shielding, water-cooled collimator for ray focusing, windowless differential ion pump for shockwave throttling and spectrum broadening (2-20 keV), and pneumatically closed and sealed gate valve for the front-end vacuum and beamline vacuum separation. At downstream of the front-end gate valve, the 6-meter long X-9 is constructed of UHV-compatible SS spool pieces, welded bellows, optical chambers, fast shutter and angle valves. To maintain the intensity and quality of undulator beam for high-resolution sampling of nano materials, the conductance-limited beamline is equipped with multiple high-capacity ion pumps, respectively mounted at cryo-ready monochromator container (dual 300 l/s pumps), XZ-staged mirror tank (one 500 l/s) and exit-slit housing (one 300 l/s). For vacuum pressure minimization, the Monte-Carlo based Molflow code was used to simulate inline assemblies and pumping units encompassing the beam chamber, and the finite-difference based Vaccalc program was used to calculate pressure distribution along the beam trajectory, starting from the photon source MGU down to the beamline end valve next to the enclosure wall. Details of calculated pressure profile versus pumping setup will be presented. (Work performed under auspices of the United States Department of Energy, under contract DE-AC02-98CH10886)

VT-TuP4 A Vacuum Quality Monitor Sensor using an Integrated Total and Partial Pressure Measurement Design, ***B.G. Olsen***, *G.A. Brucker, J. Rathbone, S. Blouch, M. Schott, K. Van Antwerp*, Brooks Automation, Inc.

We have refined and built upon the work of A.V. Ermakov and B.J. Hinch from Rutgers University to further develop a novel electrostatic ion trap sensor that is based upon the principles of autoresonant ion-ejection and detection for use in low mass range mass spectrometry applications. In addition, we have developed a practical method of integrating a total pressure measurement capability into the same sensor envelope. This highly integrated Vacuum Quality Measurement (VQM) sensor is comprised of a hot-filament ion source, electrostatic ion-trap mass separator, Shulz-Phelps based pressure sensor, and an electron multiplier ion detector that is shared for both UHV total pressure and ratiometric partial pressure detection. The VQM ion-trap sensor is capable of a 1-100amu scan rate within 70ms and has been coupled with a total pressure and partial pressure measurement update rate of 100ms. A set of sensor electronics has been developed to control, drive and process complex sensory data, and output the processed data into a usable form within the cycle time of the measurement update rate. Finally, a novel dual-filament ionization source design was incorporated into VQM sensor design to allow fast and easy field replacement of filaments.

VT-TuP5 A Compact RHEED-TRAXS Chamber Modification Design for Real Time, In-Situ Stoichiometry Analysis during MBE, ***B. Sun***, *T.L. Goodrich, K.S. Ziemer*, Northeastern University

Real-time control of MBE film growth using Reflection High Energy Electron Diffraction (RHEED) oscillations allows precise layer-by-layer growth using real-time surface structure information. Many complex functional oxides of device importance, however, require tight stoichiometry control. RHEED- Total Reflection Angle X-ray Spectroscopy (RHEED-TRAXS) can provide real-time chemical information and thus has the potential to achieve real time stoichiometry control. When incident RHEED electrons with energy in the range of 12-20 keV graze the sample surface at approximately a 2° angle, characteristic x-rays which are representative of the film surface stoichiometry are emitted. By measuring the x-rays at or close to their total reflection angle, RHEED-TRAXS is reported to probe only the top 20Å of group V elements [1].

The goal of the RHEED-TRAXS chamber modification design is to incorporate a non-UHV compatible x-ray detector into the chamber, and ensure highly accurate detector positioning within 0.01° through a 4° angle range. For real time operation, a shielding strategy that is transparent to x-rays must be developed to protect the detector from fouling during MBE processing. As a high volume of x-rays are excited by the RHEED electrons, collimation is necessary to control the incoming x-ray flux and avoid detector overload.

Our system uses a Nor-Cal PMXY-600-400-2 ±1 inch X-Y stage to achieve 0° to 4.65° angular positioning of the detector. Differential pumping with a Leybold TURBOVAC 50 L/s turbo molecular pump is used to achieve UHV compatibility. Due to limited chamber space, off-the-shelf shielding options such as shutters would cut down the detector movement and thus reduce the maximum detection angle by 50%. To avoid this, we combined detector fouling protection and collimation by mounting the detector with a custom made half-nipple covered with a removable aperture cap which provides both collimation and beryllium foil shielding support. The ability to remove the aperture cap allows the Be foil to be replaced when needed and also allows the flexibility control net x-ray flux by changing the aperture size. The system has been used for real-time study of thin film deposition by MBE, and the results will be presented.

References:

1. Braun, W. and K.H. Ploog, Real-time surface composition and roughness analysis in MBE using RHEED-induced X-ray fluorescence. Journal of Crystal Growth, 2003. 251(1-4): p. 68-72.

VT-TuP6 Method of Measuring the Volume Flow Rate of Vacuum Pumps Using CFVN, ***W.S. Cheung***, *K.A. Park, S.W. Kang, S.S. Hong, J.Y. Lim*, KRISS, Republic of Korea

Critical flow Venturi nozzles (CFVN) have been widely used in most of national metrology institutes for the precision measurement and calibration of pressurised gas flow. They enable the relaisation of the critical flow speed equal to the speed of sound at the throat of the Venturi nozzle. The critical flow is exploited in this study not only to achieve the noble stability and repeatability of gas flow but also to minimize effects of the fluctuation of upstream and down stream pressures for the measurement of the volume flow rate of vacuum pumps. These singular properties of CFVN has not fully utilized to measure the pumping speed widely used in the vacuum-related academic and industrial sectors. On the onset of this work, it became apparent that the use of CFVN unfolds new findings for precision measurement of the volume flow rate.

One of the most technical challenges in measuring the volume flow rate was to design a set of Venturi nozzles that can cover the five decades of inlet pressures from 1 bar to 0.001 mbar. Preliminary tests were carried out to examine the practical range of upstream pressure Venturi nozzles can be used within the desired measurement uncertainty of 0.2 %. They revealed that Venturi nozzles were well calibrated in the three and half decades without loss of measurement uncertainty. This observation is very significant since two different sized nozzles are sufficient to cover the desired inlet pressure test range of vacuum pumps, specifically from 100 mbar to 0.001 mbar. This point has encouraged authors to develop a new CFVN-based measurement system targeted for the measurement of the volume flow rate of vacuum pumps. This paper will introduce the details of the developed measurement system, including the configuration of mechanical parts and measurement instruments. Test results obtained from the CFVN-based measurement system are compared to those from the conventional throughput method. The pros and cons of both measurement methods are also discussed. Finally, potential applications of developed CFVN-based volume flow rate measurement technologies for vacuum pumps are briefly pointed out for instance the MFC market for gas flow control and the on-site performance analyzer of dry vacuum pumps in the semiconductor and flat display production lines.

VT-TuP7 Vacuum System for a Low Temperature Dynamic Force Microscope, ***L. Tröger***, *M. Reichling*, University of Osnabrück, Germany

We present a complete ultra-high vacuum system designated for the operation of a home built dynamic scanning force microscope for use at cryogenic temperatures. The vacuum system was designed for maximum flexibility and consists of a measurement chamber with the cryostat and two separate chambers for sample transfer and preparation.

The cryostat was modified to implement leverage for the scan head for optimum thermal coupling and vibration decoupling by eddy current damping. Thermal anchors for all electrical supply lines were installed. An in vacuo reservoir for the glass fibre for the interferometric detection system of the force microscope ensures protection from vibrations and stores spare fibre for repair. The measurement chamber was designed for best handling and optimised use of space under several technical constraints. Due to the attached cryostat functioning as cryo-pump the chamber reaches lowest pressure regimes providing best conditions not only during experiments but also for storing force microscopy tips and samples in a magazine. The preparation chamber is based on several planes with distinct focus points for preparation instruments along the main axis. The load lock is conceived for maximum exchange efficiency enabling the transfer of up to eight tips or sample at a time. This is achieved by taking advantage of the rotational degree of freedom of the transfer rod that carries a revolving magazine.

VT-TuP9 Magnetron Sputter Coater Construction and Experiments, ***A. Mezzacappa***, Vassar College

Magnetron sputter coating is a method of physical vapor deposition which occurs in vacuum with an inert gas. Production of quality coatings necessitates a rigorous approach to vacuum science. Over the course of the 2008 – 2009 academic year with support from the University of Collaboration and private donors we constructed a sputter coater modeled on a General Atomics sputter coater. The vacuum vessel is eight inches in diameter and stands approximately two feet high. It has thirteen different ports ranging in size from one and one quarter inches to eight inches. The ports accommodate a turbo pump backed by a small diaphragm pump providing 30 liter per second pumping speed, vacuum gauging, Argon and Nitrogen in-gassing, electrical feed-throughs for biasing, viewing windows, and a double tip Langmuir probe on a linear bellows. The magnetron is a two inch US Gunn capable of height adjustment. It is water cooled and powered by a MDX Advanced Energy Power Supply. The sum total of these parts is a research quality machine with immediate applications for Vassar faculty and students. Since construction of the system, we have performed the following experiments: arc discharge, copper sputter coating, spectroscopy, and spatially resolved double tip Langmuir probe scans. We have determined plasma parameters such as electron density and electron temperature. Future experiments will include coating analysis using ultrafast acoustic thin film measurements techniques. In future years, the machine will become an advanced laboratory experiment maintained by Vassar College faculty for plasma physics education and research at Vassar College .

VT-TuP10 Design, Development and Assembly of a Modified PHI 5400 XPS System for XPS/UPS Surface Analysis, ***R. Davies***, *B. Gila, C. Abernathy*, University of Florida

A surface analysis system consisting of a vacuum chamber intended for 1-inch samples was redesigned and reconfigured to accommodate 3-inch samples due to laboratory equipment limitations and financial constraints. The surface analysis system is mainly comprised of a PHI 5400 XPS system with additional functionality provided by a SPECS UVS 10/35 UV source (UPS) and a PHI 77-067 sputter ion gun (surface analysis with depth profiling). Due to budgetary considerations, a previously used PHI 5400 XPS system was purchased. The redesign of the main vacuum chamber was necessitated by the requirement of joining this system with a 3-inch sample size Varian Gen II MBE system. The redesign of the vacuum chamber intended for surface studies involved utilizing the chamber in a horizontal orientation instead of the vertical orientation typically associated with XPS systems. Due to this reconfiguration, the vacuum chamber could both integrate with the current MBE system and accommodate 3-inch samples. The reconfiguration also introduced the need to design a sample manipulation system from square one. Working with Thermionics, a manipulation system was designed that provides for 3-inch sample transport along the x, y and z axis of the Cartesian coordinate system in addition to polar and azimuthal sample rotation. This manipulation system also includes a sample heater for surface adsorption studies up to 1200°C. The customization of the sample manipulation system provided numerous capabilities for surface analysis experimentation after being attached to the reconfigured vacuum chamber. In addition, a 56-inch long vacuum chamber, which acts as a buffer extension between the surface analysis system and both the MBE system and a vacuum briefcase, was designed and assembled. All of the vacuum plumbing necessary for the differential pumping of the sputter ion gun and UV source was designed to readily combine with the reconfigured main vacuum chamber and then assembled. A vacuum briefcase has been diagrammed to provide for sample transport from a Riber MBE 2300 system to the XPS/UPS surface analysis system under vacuum.

VT-TuP11 Reconstruction of a Veeco 776 Ion Beam Deposition System With Digital Sensing and Logging Modifications, ***J. Vanderford***, *A.P. Genis*, Northern Illinois University

The purpose of this project was to document the efforts of restoring a thirty-five year old Veeco 776 vacuum deposition system equipped with a 3 inch ion beam milli-tron which was destroyed in a laboratory fire. This was a system used for the deposition of Indium Tin Oxide (ITO) used for the fabrication of ITO / P-Silicon solar cells. The fire destroyed all electronics for powering the ion source, the gas delivery system for the ion source, vacuum measurement and valve control systems, the substrate chuck heat controller, and considerable damage to the vacuum pump stack and valves Due to the age of the system, direct replacement of these components were not available. The goal of this project was not only to rebuild the vacuum system but also to incorporate a data acquisition and logging system for monitoring and recording critical process parameters associated with the operation of the system in a real time graphic interface environment. The design and engineering which was required to complete this project, as well as the re-engineering of specialized components to achieve these goals will be presented.

VT-TuP12 Ultra-Clean Magnetron Sputtering System for Materials Research and Education, ***H. V Nampoori***, *G.J. Mankey*, University of Alabama

Construction and implementation of a multi-target magnetron sputtering system with substrate carousel is reported in this poster. The system has four magnetrons arranged on a circle and facing up, to enable deposition of multilayers for applications such as magnetic media, tunnel junctions and MRAM devices.

Up to twelve substrates can be loaded into the system on a rotating carousel. In addition, a lifter assembly can be used to move samples between positions on the carousel fitted with shadow masks. The bottom up sputtering is achieved in stainless-steel, bell-jar chamber with a rotary vane pump and Cryotorr 8 combination. With internal bake-out heaters using two 600 W halogen bulbs, a base pressure of 2 x 10^{-8} Torr is achieved. Argon pressure during sputtering is controlled using a MKS flow controller and Adaptorr butterfly valve with a Baratron gauge. Each magnetron has a shutter controlled by a Durant programmable timer. Substrate heating during deposition could be achieved using a 150 W halogen projector lamp located above each magnetron source. A quartz crystal microbalance thickness monitor can be used to determine the deposition rate for each gun. In addition, the carousel has integrated permanent magnets designed to grow magnetic thin films with induced uniaxial anisotropy.

This poster will describe the motivation and design of the system and present some preliminary results. The results will highlight the uniqueness of the system design for a manually-operated, simple and user-friendly machine.

This work was supported in part by the National Science Foundation MRSEC Grant DMR-0213985.

VT-TuP13 Outgassing Measurement of Ion and Getter Pumps at UHV Regime, ***G.Y. Hsiung***, *C.M. Cheng,* NSRRC, Taiwan, *J.R. Chen*, NSRRC and NTHU, Taiwan

The combination of ion pumps and getter pumps have been used for the advanced pumping at UHV regime of a pressure below 10 nPa. The effective pumping speed of ion and getter pumps is limited at UHV pressure due to the outgas of the materials inside the pumps such as H_2 and CO or that evolved from the surface reactions during or after pumping such as CH_4. Besides, the outgas of the noble gas such as He or Ar buried inside the cells of ion pumps as well as the Kr or Ar from the coated film of getter pumps is regarded as one of promising limit of pumping speed. The measurement of outgas of ion and getter pumps is performed by pressure build up method. The cleaning process for reduction of the outgas of the ion and getter pumps are evaluated.

VT-TuP14 Study of Secondary Electron Yield for KEKB Positron Ring, ***S. Kato***, *M. Nishiwaki*, KEK, Japan

In order to mitigate electron cloud instability in high-intensity positron and proton accelerators, material surface with a low secondary electron yield (SEY) for the beam ducts is highly desired. In-situ SEY measuring system in the straight section of the KEKB positron ring was reported where one can measure SEYs of sample coupons exposed to electron cloud during the KEKB operation. In this study we aim to develop a mobile UHV system for sample coupon transfer from an arc section of the positron ring to a load lock chamber of XPS at our laboratory in order to carry out SEY measurements and surface analyses without exposing coupons to the air. There are two sample ports with a size of 8x8 mm^2 at the side and the bottom of the positron beam duct for comparison. While both of samples are exposed to electron cloud caused by strong synchrotron light from a bending magnet of the ring, the light directly hits only the sample positioned at the side port. Sample coupons exposed to electron cloud can be transferred to UHV suitcases 1 and 2 through isolation gave valves installed between the beam duct and the suitcases. An amount of electron cloud is measured with the electron monitor. The UHV suitcase consists of a gate valve, linear and rotary motion drives to transfer the coupons, an ion pump with its power supply and drive batteries. The total weight is about 10kg. Two suitcases are almost identical. These suitcases are moved and connected to the second load lock chamber where the coupons up to 12 can be kept in UHV before the measurement. In this paper, the detail of the SEY measuring system is mentioned with its experimental results after a long time exposure of the coupons to the electron cloud during the KEKB operation.

VT-TuP15 Energy Consumption Characteristics of Low Vacuum Dry Pumps in Semiconductor Manufacturing, ***J.Y. Lim***, KRISS, Korea, *H.Y. CHoi,* LOTVacuum, Korea, *W.S. Cheung, J.H. Shin, S.B. Kang, Y.-H. Shin*, KRISS, Korea

Recent SEMATECH and SEMI studies showed that 50~60% of equipment power is used for vacuum pumps. Currently vacuum pump suppliers have responded by reducing power consumption and cooling water flow requirement in energy consumption at the component level. Actual process studies showed that for some processes, the energy consumption level did not change significantly during idle and processing operation modes. However, specified studies in experimental scale to characterize the energy consumption pattern have not been reported yet.

We have performed a simulation study to characterize energy consumption pattern in the idle and process modes.

The pressure range of about 0.1 to 50 mbar for 7 minutes was assigned to the simulated process mode, meanwhile the pressure of <0.1 mbar for 3 minutes to the idle mode. The integrated characteristics evaluation system for dry vacuum pumps has been utilized to gather the dry pump characteristics data for the simulation. The evaluation system exploits the constant volume flowmeter to measure the mass flow rate real-timely in standard level, and facilitates the evaluation of spatially averaged sound power levels using a reverberation chamber. Roots, claw, classical screw, and multi-stage type vacuum pumps supplied from the manufacturers have been evaluated using the evaluation system in terms of ultimate pressure, pumping speed, power consumption, vibration, sound power as well as nitrogen purge, cooling water rate from the single pump monitoring system in time-synchronized mode. This study includes the application of the SEMI S23-0705 standards – A Guide for Conservation of Energy, Utilities and Materials Used by Semiconductor Manufacturing Equipment.

The estimated power consumption per pump per year was ranged from 10 to 30 MWh and 15 to 50 MWh for 600 ~ 1200 m^3/h dry pumps in idle and processing modes, respectively. The utility energy consumption was also ranged from 5 to 10 MWh and 10 to 30 MWh, respectively. More specific energy consumption patterns with respect to the pressure are also presented. In this work we suggest that the correlation mechanism dependant on the actual process lines should be carefully analyzed and furthermore understood, for example, the relationship between cooling water flow rate and temperature variation during processes.

VT-TuP16 Development of a Pulse Motor Driven All Metal Valve for a Static Expansion System, ***K. Arai***, *T. Tomita, H. Akimichi, M. Hirata*, NMIJ/AIST, Japan

A static expansion system generates standard pressures for the calibration of a spinning rotor gauge and a capacitance diaphragm gauge. Valves are important parts for the system. All metal pneumatic valves are used for an automatic operation. However, the pneumatic valve closes so rapidly (<1 s) that the undesirable differential pressure between both sides of the valve is seemed to be induced by pushing gas. In order to clarify it, a test system consists of 45 m chamber and 3000ml chamber connected by the pneumatic valve was set up. The 13 Pa of differential pressure at the 100 kPa of line pressure was generated by closing the valve. The pressure decreased to 1.5 Pa by elongating the valve closing time, 150 s, by the control of the flow rate of the pneumatic line. However, the repeatability of the valve closing was not sufficient.

Pulse motor driven all metal valve was developed: (1) The motor drive part is attached to a commercial available valve, (2) A valve stem is driven by the pulse motor via a torque-limiter, springs, and a valve shaft, (3) The valve shaft position at closing the valve is always same by using the position sensor, (4) Springs are used to close the valve with the same torque, (5) To avoid the increase of the temperature of the valve body, the motor is operated only for the valve operation and 50 cm away from the body, (6) The torque-limiter is put between the motor and the shaft not to break the valve by the over torque.

The stem speed was controlled ranging from 0.1 to 0.008 mm/s (closing time: 25 ~ 300 s). The differential pressure could not be eliminated by slowing the stem speed. The smallest pressure was 1.4 Pa at the 100 kPa of the line pressure. Taking into account the pressure and the test chamber volume, 1.4 Pa is corresponding to the 0.0006 ml volume change of the valve. The mechanism of the undesirable differential pressure during the valve closing can be analyzed by measuring the detailed pressure change as a function of the time and the position of the stem.

VT-TuP17 A Novel Reactor Setup for Surface and Gas-Phase Diagnostics during Atomic and Molecular Layer Deposition, ***B. Jariwala***, *V. Rai, C.V. Ciobanu, S. Agarwal*, Colorado School of Mines

In this presentation, the authors will describe the design of a versatile reactor setup with multiple in situ diagnostics to study the surface reaction mechanisms during atomic and molecular layer deposition. The setup consists of two vacuum chambers: the first chamber is equipped with real-time attenuated total reflection Fourier-transform infrared (ATR-FTIR) spectroscopy and quadrupole mass spectrometry, while the second chamber is equipped with a quartz crystal microbalance. Both chambers are connected to multiple in-house-built bubblers to supply different precursors. In addition, each chamber is equipped with an inductively-coupled, radio-frequency plasma source that is in line of sight with the substrate for plasma-assisted atomic layer deposition (ALD). The precursor delivery into the chamber is controlled through solenoid valves operated via Labview. The infrared analysis chamber is ideal for observing the surface species and the gas phase products during each half-reaction cycle. However, due to the multiple diagnostics, which require several ports, the chamber volume is large resulting in long precursor exposure and purge cycles. On the other hand, the second process chamber is a hot-wall tubular reactor with a small volume, which allows shorter reaction cycles enabling the deposition of films that are several 10s of nm in thickness: these thicknesses are required to obtain enough sensitivity for ex situ IR and x-ray diffraction analysis. We will specifically present results for the thermal and plasma-assisted ALD of TiO_2 that will demonstrate the synergistic utilization of each diagnostic tool to unravel the specific surface reactions during film growth.

VT-TuP18 A Method of Transfering Parts Rapidly Into and Out of a High Vacuum Environment, ***E. Trillwood***, CEO Electron Beam Engineering

The novel device uses a piston and a cylinder, both with seals to penetrate the wall of a high vacuum processing chamber. The piston is hollowed out for a portion of its length and the component to be processed in the chamber is placed in this cavity, or breach. The piston, as it moves into the chamber, passes over a pre pumping station which is fitted with a two stage mechanical pump to pre evacuate the breach. Since the volume closely fits the component the evacuation time is usually one second or less. When the component enters the chamber "volume sharing" occurs and the resulting pressure rise is very small and rapid as the chamber high vacuum pumps the differential pressure between the breach and the chamber.

The seals are placed in such a manner as to isolate the atmosphere, the pre pumping and the chamber vacuums from each other at all times in the cycle.

On completion of the process the piston is withdrawn from the chamber and the breach returned to atmosphere.

Apart from the speed of operation the system has the advantage of being self valving and if a second breach or dummy piston is added to the opposite side of the chamber the forces on the piston due to atmospheric pressure are equalized and the force required to transfer the piston is greatly reduced.

This system has been used successfully in production Electron Beam Welding but has many other potential uses where ease and speed of loading and unloading relatively small parts into a vacuum chamber is requied.

Applied Surface Science
Room: C1 - Session AS+NS-WeM

Nanoparticle and Nanoscale Surface Chemistry II
Moderator: D.J. Gaspar, Pacific Northwest National Laboratory

8:00am **AS+NS-WeM1 Size-dependent Properties and Surface Chemistry of Metal Oxide Nanomaterials***, **V. Grassian***, University of Iowa

Both natural and engineered oxide nanomaterials play important roles in environmental processes. In the case of engineered nanomaterials, the surface properties can be tailored for a number of different environmental applications including deNOx catalysis and carbon dioxide removal and conversion. For naturally occurring oxide nanomaterials, e.g. iron oxides, the size dependent properties and surface chemistry will impact biogeochemical cycles. In this talk, some specific examples of the size-dependent properties and surface chemistry of both natural and engineered metal oxide nanomaterials (e.g. titanium dioxide and iron oxide) in environmental processes will be discussed.

8:20am **AS+NS-WeM2 XPS and SEM/STEM Characterization of Silver Nanoparticles Formed from the X-ray-Induced and Thermal Reduction of Silver Behenate***, **B.R. Strohmeier**, K.L. Bunker, C. Lopano, J. Marquis, Jr., J.D. Piasecki, K. Bennethum,* RJ Lee Group, Inc.*, R.G. White, T.S. Nunney,* Thermo Fisher Scientific, UK, *R.J. Lee*, RJ Lee Group, Inc.

This study is the first reported use of X-ray photoelectron spectroscopy (XPS) to characterize the organometallic compound silver behenate and its X-ray-induced and thermal reduction. Silver behenate is a long-chain silver carboxylate, $CH_3(CH_2)_{20}COOAg$, that crystallizes as a dimer in a head-to-head configuration. Various silver compounds, including silver behenate, are used as primary components in commercially available photothermographic (PTG) and thermographic (TG) imaging elements. Individual particles of silver behenate powder typically exist as plate-like crystals with surface dimensions of 0.2-2 µm and thicknesses of 100 nm or less. Imaging in PTG and TG devices is based on the formation of silver metal nanoparticles in the 5-30 nm range (and larger aggregates) by the thermal reduction of silver behenate dispersed in a binder incorporated with toner and development chemistry. Silver behenate has also found use as a standard reference material for low-angle calibration of X-ray diffraction instruments because its crystal structure produces a unique multi-peak diffraction pattern.

In this study, the X-ray-induced reduction of silver behenate during exposure to monochromatic Al Kα X-rays in a micro-XPS instrument was investigated as well as its thermal reduction at 100 °C and 250 °C. The X-ray induced decomposition of other silver carboxylates (silver acetate, silver benzoate, and silver trifluoroacetate) was also investigated for comparison to the behavior of silver behenate. In addition, a combined high resolution scanning electron microscope/scanning transmission electron microscope (SEM/STEM) was used in this study to provide complementary morphological information to the XPS results.

Quantitative XPS analysis of silver behenate was consistent with the theoretical C:O:Ag atomic composition. However, brown discoloration of silver behenate powder begins within a few seconds of exposure to Al Kα X-rays and increases significantly with time. Noticeable changes to the XPS spectra and the observed surface composition begin to occur after about 30 minutes of X-ray exposure. Prolonged exposure to Al Kα X-rays resulted in significant changes in the C 1s, O 1s, and Ag 3d peak shapes and positions. Changes in the XPS spectra indicated that exposure to Al Kα X-rays results in the formation of silver metal particles and decomposition of the carboxylic acid potion of the molecule to hydrocarbon species. Thermal reduction of silver behenate powder produced similar changes in the XPS spectra. This study demonstrated that XPS and SEM/STEM are complementary techniques for investigating the chemical composition, morphology, and decomposition of nanomaterials.

8:40am **AS+NS-WeM3 Surface Chemistry of Deuterium Terminated Silicon Nanocrystals and Effect of Surface Passivation on Photoluminescence***, **N. Salivati***, J.G. Ekerdt*, University of Texas at Austin

Although silicon nanostructures exhibit size dependent light emission, which can be attributed to quantum confinement, the role of surface passivation has not yet been fully understood. Since the ratio of surface atoms to the total number of atoms is large in nanoscale systems, surface effects play an important role in determining the electronic properties. Uncompensated dangling bonds at the surface establish localized defect states within the forbidden gap of silicon nanocrystals, providing sites for non-radiative recombination of excitons. Defect states are also associated with surface reconstructions that minimize the number of dangling bonds but result in severe distortion of the surface bonds. An effective way of capping the remaining dangling bonds is by using atomic hydrogen or deuterium. Si nanocrystals less than 8 nm in diameter are grown on SiO_2 surfaces in an ultra high vacuum chamber and the as grown surfaces are exposed to atomic deuterium. Desorption spectra are interpreted using analogies to Si (100). TPD spectra show that the nanocrystal surfaces are covered by a mix of monodeuteride, dideuteride and trideuteride species. The manner of filling of the deuteride states on nanocrystals differs from that for extended surfaces as the formation of the dideuteride and trideuteride species is facilitated by the curvature of the nanocrystal. Etching of the nanocrystal surface is observed during TPD, which is a confirmation of the presence of trideuteride species on the nanocrystal surface. No photoluminescence (PL) is observed from the as grown unpassivated nanocrystals. As the deuterium dose is increased, the PL intensity also begins to increase. Strong PL is observed only when the nanocrystals are covered with trideuteride species. The trideuteride species helps in reducing the surface stress and this is expected to enhance PL. When the deuterium dose is increased beyond a point the surface structure breaks down and amorphization of top layer of the nanocrystal takes place. Amorphization reduces the PL intensity. Finally, as the nanocrystal size is varied, the PL peak shifts, which is characteristic of quantum confinement.

9:00am **AS+NS-WeM4 Experimental Characterization of CdSe/ZnS Core/Shell Quantum Dots Encapsulated with Poly(maleic anhydride-*alt*-1-tetradecene)***, **G. Zorn***, S.R. Dave, T. Weidner, X. Gao, D.G. Castner*, University of Washington

Semiconductor nanocrystals (Quantum Dots, (QDs)) have started to play a pivotal role in molecular labeling, cancer diagnostics and tumor imaging due to their quantum mechanical and electronic characteristics. These characteristics give them unique optical properties such as size-tunable emission profiles, broad excitation spectra, long fluorescence lifetimes, large Stokes shifts and high quantum yields. The most common QD type is a CdSe/ZnS core - shell structure surrounded by hydrophobic ligands[1]; but for biological applications, QDs have to be transferred into aqueous solutions and require specific techniques for the conjugation of small peptides or antibodies onto their surfaces. In this context, a promising and widely used approach is, to encapsulate the nanocrystals with an amphiphilic polymer[1,2]. Still, there are only few reports regarding characterization of absorbed polymer and theoretical analyses are typically based on simple geometric models.

This work is focused on characterizing the amount of the amphiphilic Poly(maleic anhydride-*alt*-1-tetradecene) (PMAT, Mw~9000) adsorbed onto a TOPO-coated CdSe/ZnS QD, as well as analyzing the polymer structure and the TOPO – PMAT interaction. An insight into the elemental composition of the nanocrystals before and after PMAT encapsulation is provided along with the orientation of the surrounding organic components. EDAX, XPS and ToF-SIMS suggest the QDs are comprised of non-stoichiometric Cd-enriched QDs with a ~0.5 monolayer ZnS shell. SFG C-H stretching of the CdSe/ZnS nanocrystals before PMAT encapsulation shows that there is a significant degree of orientational order in the TOPO film. Moreover, after PMAT encapsulation SFG C-H stretching indicates a certain degree of order in the PMAT polymer layer. Finally, from XPS analysis the number of PMAT molecules per QD is estimated to be ~7 to 1.

Reference:

1. Smith, A. M.; Dave, S.; Nie, S.; True, L.; Gao, X., *Expert Rev. Molec. Diagnos.* **2006,** 6, 231-244.

2. Rhyner, M. N.; Smith, A. M.; Gao, X.; Mao, H.; Yang, L.; Nie, S., *Nanomedicine* **2006,** 1, 209-217.

9:20am **AS+NS-WeM5 2009 AVS Albert Nerken Award Lecture - Reactivity of Nanoparticles and Other Surface Controlled Properties of Materials**, ***D.R. Baer****, *J.E. Amonette, M.H. Engelhard, J. Liu, P. Nachimuthu, C.M. Wang,* Pacific Northwest National Laboratory*, J.T. Nurmi, P.G. Tratnyek,* Oregon Health and Sciences University*, M. Kaur, Y. Qiang*, University of Idaho **INVITED**

Many materials properties are controlled by surface reactions, including those associated with cracking, dissolution, and corrosion. In each of these cases surface reactions alter the functional properties of the materials.

---

* Albert Nerken Award Winner

Detailed analysis of surface reactions in relation to the material environment has been required to understand the mechanisms involved in these processes. Many of the analysis approaches used to understand dissolution, cracking corrosion and other complex material-environment interactions are relevant to the study of some types of nanoparticles. The objective of our current research is to obtain fundamental information about the physical and chemical transformations that occur on and within mineral oxide nanoparticulates due to electron transfer reactions and other interactions with their local environment, including solution contaminants such as chlorinated hydrocarbons. The nature of the reactive surfaces, the accessibility of reactive sites, and the structures of the surface and interface layers often change significantly as particles respond to and react with their local environment (e.g. surface structure alterations, phase changes, passive layer formation …). Although geochemically induced changes occur for bulk materials, the nature and rate of these changes can be more dramatic for nano-sized mineral phases. Our research focuses on obtaining information about these geochemically mediated transformations and how they alter particle reactivity, electron availability and particle mobility. Our research includes 1) synthesis of well-defined nanoparticles (NPs), 2) characterization of their surface and bulk composition as well as physical and electronic structure (prior to and following reaction measurements), and 3) *in situ* real-time and batch measurements of NP properties and reactivity in vacuum and solution. We will report on studies showing the impact of natural organic material (NOM) coatings on the through soil transport and reactivity of iron nanoparticles as well as the role of metal dopants on reactivity and solution aging. We have found that NOM can enhance the transport of iron metal-core oxide-shell nanoparticles through a soil column, decreasing the numbers of particles retained in the soil. We have followed up these observations and examined the impact of NOM coatings on the particle aging. Additional studies are examining the impact of S doping on particle reactivity and aging. These studies involve application of a variety of analysis methods to the particles, including XPS, XRD and TEM as well as batch and in situ measures of chemical reactivity and measurements of particle transport through soil columns.

10:40am **AS+NS-WeM9 Surface Characterization and Simulation of Self-Assembled Monolayer Functionalized Gold Nanoparticles**

S.D. Techane*, L.J. Gamble,* University of Washington*, M.H. Engelhard, D.R. Baer,* Pacific Northwest National Laboratory*, D.G. Castner*, University of Washington

In this research gold nanoparticles (AuNP) are used as model nanoparticles and self-assembled monolayers of alkyl thiols as model organic ligands to create functionalized NP with a variety of surface chemistries. The AuNP size and thiol chain length are varied to study their effects on the properties of the AuNP. Our aim is to create a series of well-defined functionalized AuNP for use in complex biological applications and to use the AuNP-SAMs as standard samples to develop XPS (X-ray photoelectron spectroscopy) data analysis methods for coated NP characterization. We have synthesized and characterized four chain lengths of COOH-SAMs (C6, C8, C11, C16 carboxylic thiols) on various sizes of AuNPs (diameter =14nm, 25nm, 40nm) and flat gold surfaces using the surface sensitive techniques of XPS and ToF-SIMS. Many of the trends expects for increasing SAM thickness are observed. In addition data shows that particle size (surface curvature) had an effect on the XPS and ToF-SIMS measurements. Complementary ATR-FTIR (attenuated total reflectance FTIR) measurements were done to characterize the SAM ordering and crystallinity. As SAMs length increased the CH_2 stretching vibration frequencies (υCH_2) decreased on both AuNPs and flat-Au surfaces. For a given chain length SAMs the υCH_2 also decreased as the AuNPs particle size decreased indicating that longer chain SAMs on the smaller AuNPs (i.e. 14nm-C16 COOH-SAMs) have the most crystalline surface structure. As the XPS C/Au atomic ratio depends on the structure of the SAMs as well as the take-off angles (which range from 0 to 90° for particles) there is a need to develop XPS data analysis methods that accurately account for curved NP surfaces. SESSA (Simulated Electron Spectra for Surface Analysis) and QUASES (Quantitative Analysis of Surfaces by Electron Spectroscopy Software) have been used to simulate the experimental XPS results as a function of take-off angle for COOH-SAMs on flat-Au surfaces. Quantities such as SAM density, thickness, surface roughness and instrumental parameters were tuned in SESSA to optimize agreement between simulated and experimental XPS compositions for SAMs on flat Au surfaces. SESSA results were compared with experimental measurements taken from 3 different XPS instruments: Quantum (EMSL/PNNL), Kratos and S-probe (NESAC/BIO). Approaches are being used to apply SESSA and QUASES to analysis of the particle data.

11:00am **AS+NS-WeM10 Nanocerium Oxide as Antioxidant – Role of Environment and Surface Coating on the Interaction with Reactive Oxygen Species**

A.S. Karakoti*, S. Singh, A. Kumar,* University of Central Florida*, S.V.N.T. Kuchibhatla,* Environmental and Molecular Sciences Laboratory*, W.T. Self, S. Seal*, University of Central Florida

The astounding progress of nanotechnology in numerous areas of science and biotechnology is posed with a significant challenge of overcoming the nanotoxicological properties of these materials. More often than not nanomaterials produce oxidative stress when exposed to cellular environment leading to rapid cell death. While several nanomaterials are linked with oxidative stress; cerium oxide nanoparticles (CNPs) show an inverse behavior by scavenging the reactive oxygen species (ROS) thereby reducing the oxidative stress and acting as antioxidant oxides. The antioxidant properties of nanoceria originate from its redox properties, surface chemistry and nanoparticulate size. It was observed that a critical ratio of Ce^{3+}/Ce^{4+} was required for exhibiting better antioxidant properties. Due to the reversible nature of its redox properties i.e. CNPs can regenerate its active radical scavenging oxidation state upon interaction with ROS such as peroxide and superoxide. To increase the biocompatibility and cell permeability characteristics, CNPs were synthesized in biocompatible mediums such as polyethylene glycol (PEG) and dextran. Cell viability studies showed excellent biocompatibility of the CNPs synthesized in biocompatible mediums. The antioxidant property of CNPs in these medium was compared to the water based CNPs using classical superoxide dismutase (SOD) model and it was found SOD mimetic activity was unaltered by the presence of organic coating on CNPs. Reaction of hydrogen peroxide with CNPs was used to compare the changes in oxidation state of CNPs upon interaction with peroxide species. While both PEG and dextran showed tunable redox property; it was found that the redox property of PEG based CNPs were acutely affected by medium due to change in the polarity and dielectric constant of the medium. A clear indication of formation of charge transfer complex was found with PEG while no such complex was observed with dextran. Additionally CNPs synthesized in PEG (5 – 80 vol% PEG) showed concentration dependent red shift in the formation of CNP-PEG charge transfer complex. Upon dialysis it was found that the polymer formed a stable coating on the surface of CNPs and the surface coating was linked to the observed differences in the regeneration of the oxidation state of nanoparticles. High resolution transmission electron microscopy, Fourier transform infra red spectroscopy and UV-visible spectroscopy were used to characterize the particle size, nature of coating and dynamic oxidation state of nanoceria. X-ray photoelectron spectroscopy used to probe the surface chemistry and oxidation state of CNPs.

11:20am **AS+NS-WeM11 Dynamic Nature of Cerium Oxide Nanoparticles – Influence of Aging and Local Environment**

S.V.N.T. Kuchibhatla*,* Pacific Northwest National Laboratory*, A.S. Karakoti,* University of Central Florida*, C.H. Windisch Jr., P. Nachimuthu,* Pacific Northwest National Laboratory*, S. Seal,* University of Central Florida*, S. Thevuthasan, D.R. Baer*, Pacific Northwest National Laboratory

Cerium oxide nanoparticles (CNPs) are a subject of increasing attention in the biomedical field in addition to many traditional applications such as catalysis, sensors and fuel cells. Most of the applications of CNPs are driven by the oxygen buffering capability, which in turn is guided by the ability of cerium to switch between 3+ and 4+ oxidation states. The thermodynamic stability of oxygen vacancies in the particles below 10 nm makes this switching more efficient. Motivated by this fact, the CNPs have been used to study their biological response (cell longevity, toxicity and related aspects) and the preliminary results have shown excellent radical scavenging ability. It has also been noted that the CNPs can effectively regenerate the active redox state. However, an unequivocal mechanism is still not reported.

We have studied, *in situ*, the influence of time (aging) and local environment (chemistry) on the chemistry and structure of CNPs. With the help of UV-Visible and Raman spectroscopy along with microXRD measurements, we have observed that the CNPs are highly dynamic in nature and respond, through changes in chemical state and possibly structure, to the variations in their local environment as a function of time. Raman data with support from XRD and some XPS results suggests that the CNPs undergo the transformation between 3+ and 4+ oxidation state through the formation of a *"peroxide-complex"* in presence of hydrogen peroxide, which as a function of time leads to the formation of cerium oxide nanoparticles, regeneratively. Interaction of CNPs with hydrogen peroxide was used as a model system for explaining the regenerative nature of CNPs in biological applications. Various results from this study, along with the size dependence of the transitions, will be presented while discussing the merits of the findings and their implications to the bio-medical applications.

11:40am **AS+NS-WeM12 Characterizing Environmentally Induced Changes in Nanoparticle Surface Chemistry***, A.N. Mangham, P. Wiecinski, S.P. Yang, K.M. Louis, R.E. Peterson, W. Heideman,* ***A. Pedersen****, R.J. Hamers*, University of Wisconsin-Madison

The routes of exposure and toxicity of nanoparticles in the environment are expected to be strongly affected by the nature of surface chemical groups exposed on the outside of the particles. We have developed a laboratory-based method that simulates oxidative processes in the environment, and have applied this method to investigate the resulting changes in surface chemistry of "bare" and ligand-functionalized nanoparticles. Using CdSe as a model system, we have compared the behavior of ligands bearing different surface anchor groups including carboxylic acid groups, amines, and phosphonates. Wrapping these ligand-modified nanoparticles with amphiphilic polymers can enhance the particle stability as well as the luminescence efficiency. Surprisingly, the type of surface anchoring group has a strong effect on the stability of even the polymer-wrapped nanoparticles. Using infrared, Raman, and x-ray photoelectron spectroscopies, combined with thermogravimetric analysis, we related the differences in stability of the nanoparticles to the chemical and physical structure of the ligands. Our results show that the most thermally stable groups do not necessarily provide the best protection against degradation. As time permits, the influence of the surface chemistry on the nanoparticle toxicity using a zebrafish model will be presented and discussed.

Applied Surface Science
Room: C2 - Session AS-WeM

Electron Spectroscopies
Moderator: R.L. Opila, University of Delaware

8:00am **AS-WeM1 Probing Photoinduced Charging in CdS and CdSe Films by Dynamical XPS Measurements***, H. Sezen,* ***S. Suzer***, Bilkent University, Turkey

Photoconductive materials have gained renewed interest in recent years due to the advancements in controlling their electronic and optical properties, which exhibit strong size, shape and chemical composition dependence. Recently, we have developed a technique for recording the shifts in the positions of the XPS peaks in response to different forms of electrical stimuli for probing dynamics of charging/discharging processes in thin dielectric films, which we have named as Dynamical XPS. In the present contribution, we introduce photoillumination as an additional form of stimuli and investigate the combined optical + electrical response of thin CdS and CdSe films deposited on silicon substrates containing ca. 5 nm thermal oxide layer. Modulation of the electrical signals in the forms of square, sinusoidal and triangular waves at different frequencies enables us to extract some dielectric properties of the SiO_2 and CdS (or CdSe) surface structures both under and without photoillumination. Experimental results will be presented, discussed, and compared with those of simulations.

8:20am **AS-WeM2 Energy Filtered PhotoElectron Microscopy***, K. Winkler,* ***M. Maier****,* Omicron NanoTechnology GmbH, Germany*, M.E. Escher,* Focus GmbH, Germany*, B. Kroemker, D. Funnemann*, Omicron NanoTechnology GmbH, Germany

Photoelectron emission microscopy (PEEM) in combination with a high-resolution energy filter (ΔE in the 100meV regime)[1] is a non-destructive and versatile surface characterisation technique with the ability to solve upcoming scientific metrology issues [2].

Looking at the Roadmap for Semiconductors today, scaling down of devices faces growing complexity of the related issues. To overcome these issues often requires detailed analysis at a local scale where understanding of materials in the form of small objects or patterns is of great importance. Hence the need for new spatially-resolved, non-destructive and comprehensive analysis tools becomes clear.

To identify the chemical compounds in a local sample area, energy-filtered PEEM is a very valuable metrology tool combining high spatial resolution with high-resolution spectroscopy. Continuous improvements of PEEM instruments nowadays enable local nano-spectroscopy with the highest lateral resolution in convenient laboratory conditions [3]. Imaging XPS with unsurpassed lateral resolution and quantitative analysis of the local work function allow for a detailed understanding of the surface chemistry, including locally resolved doping effects [4] on small structures used for semiconductor devices and even smaller silicon nano-wires[5].

In addition, recent experiments have shown the feasibility for a new class of experiments for band structure analysis. Advanced spectroscopic PEEM instruments allow a new approach to analyse the electronic structures of samples. Thus band structure mapping with a large acceptance angle of ±90° without the need for eucentric sample rotation becomes possible [6]. Together with full control over the analysed local area, the technique is ideally suited to investigate the electronic properties of single grains or small devices. Hence, this method opens up the path to a new class of experiments allowing e.g. dedicated local band structure tailoring.

1. M. Escher et al. J. Electron. Spectrosc. Relat. Phenom. ***144*** *(47), pp. 1179-1182 (2005).*

2. M. Senoner et al. Jurnal of Surface Analysis ***12****, pp 78-82 (2005).*

3. O. Renault et al., Surface Science. ***601****, pp 4727 - 4732(2007).*

4. N. Barrett et al. submittet to J Phys Condens Matter (2008) .

5. A. Bailly et al. Nano Lett., ***8*** *(11), pp 3709–3714 (2008).*

6. B. Krömker et al. Rev Sci Instrum. ***79****, 053702 (2008).*

9:00am **AS-WeM4 Some Problems of Quantitative Applications of High (up to 15 keV) Energy X-ray Photoelectron Spectroscopy***,* ***L. Kover***, Institute of Nuclear Research of the HAS, Hungary

X-ray photoelectron and Auger spectroscopy, using hard X-rays for excitation and high energy resolution (HAXPES), due to the availability of the 3rd generation synchrotrons and advanced electron spectrometers, has shown a spectacular development recently allowing to utilize its non-destructive capability for providing a deeper insight into the bulk electronic structure of solids and the chemical composition of buried layers and interfaces lying at depths of several tens of nm. Quantitative analytical applications of HAXPES e. g. for studies of materials with new, important functions and complex physical, electronic and chemical structure are highly desired, however, some conditions are significantly different compared to the case of the conventional XPS. Although surface excitations and elastic electron scattering are playing a smaller role at higher electron energy and the inelastic background becomes less important, the low photoionization cross sections request a careful design of the experiments, non-dipole effects influencing the angular distribution of photoelectrons are non-negligible and effects of atomic recoil should be taken into account in the case of low atomic number components when looking at chemical shifts or energy broadening of core photoelectron lines. In addition, the available data for parameters (e. g. parameters characterizing electron transport in solids in the 2-15 keV electron energy range) necessary for quantitative chemical analysis using HAXPES are rather sparse and our present knowledge is limited concerning the role of intrinsic (core hole induced) excitations. In this contribution the magnitude and the energy dependence of physical parameters (derived from experiment or estimated using model calculations) relevant for quantitative applications of HAXPES are discussed together with new experimental data and simple models proposed for describing high energy photoinduced electron spectra. Acknowledgements: The support of the HASYLAB/DESY and the European Community under Contract RII3-CT-2004-506008 (IA-SFS) as well as by the Hungarian project OTKA 67873 is gratefully acknowledged.

9:20am **AS-WeM5 Hydrogen Quantification at Surfaces by Electron Spectroscopy***,* ***F. Yubero***, CSIC, Spain **INVITED**

The quantification of H at the surface is a subject of key importance. However, direct quantification of this element at the surface region (<2-3 nm) is not an easy task. Note for example that H does not show photoemission peaks in standard surface analysis by XPS. An indirect way to quantify it is by means of High Resolution Electron Energy Loss Spectroscopy, but only those H atoms participating in the vibrational absorption spectra would be observed. It is also possible H quantification with surface sensitivity by means of Nuclear Reaction Analysis, but this technique is not easily available.

Recently it has been proposed a method to quantify the H content at the surface of a-C:H samples based in the analysis of elastically backreflected electrons with primary energies about 1500 eV [1,2]. It is based on the fact that the recoil energy of the incident electrons depends on the atomic mass of the atoms located at the surface that act as scatter centres. Fairly consistent analysis were found for a-C:H materials and polymer surfaces. [1,2]. This new strategy of analysis has also been use to distinguish between H and deuterium (D) at the surface of ice water. The possibilities of this new technique, in combination with standard X-ray photoemission, for example for the study of polymer surfaces that have been labelled with either H or D, will be discussed.

[1] F. Yubero, V.J. Rico, J.P. Espinós, J. Cotrino, A.R. González-Elipe, Applied Physics Letters 87, 084101 (1-3) (2005)

[2] V.J. Rico, F. Yubero, J.P. Espinós, J. Cotrino, A.R. González-Elipe, D. Garg, S. Henry, Diamond and Related Materials 16, 107-111 (2007)

10:40am **AS-WeM9 Hot Electron Transport Properties of Thin Copper Films Using Ballistic Electron Emission Microscopy**, ***J.J. Garramone***, *J.R. Abel, I.L. Sitnitsky,* University at Albany*, L. Zhao, I. Appelbaum,* University of Maryland*, V.P. LaBella*, University at Albany

Copper is widely used material for electrical interconnects within integrated circuits. In addition it has been recently utilized as a base layer for hot electron spin injection and readout into silicon[1]. Integral to both their application is the knowledge of the electron scattering length. Surprisingly little work exists that directly measures the scattering length of electrons in copper. One method for studying hot electron transport on the nanometer length scale is ballistic electron emission microscopy (BEEM). BEEM is a three terminal scanning tunneling microscopy (STM) based technique, where electrons tunnel from a STM tip into the grounded metal base of a Schottky diode[2]. The electrons that transverse the metal overlayer and surmount the Schottky barrier are measured as the BEEM current by a backside contact to the semiconductor.

In this study we used BEEM to measure the hot electron attenuation length of copper on Si. The samples consists of Au/Cu/Si(001) Schottky diodes and the measurements were taken at 77K under UHV conditions. The Au capping layer is used to inhibit the growth of copper's native oxide. Analysis of BEEM current as a function of tip bias yield a Schottky barrier height of 0.64±0.02 eV. The barrier height is in good agreement with previous current-voltage measurements[3-5]. This, along with Rutherford backscattering spectrometry, indicates that we are measuring the Cu/Si Schottky height and have the ability to measure the attenuation length of copper by measuring the BEEM current as a function of Cu thickness. The measured hot electron attenuation length of Cu is 41.64±1.2 nm at a tip bias of 0.9 eV. The attenuation length decreases monotonically with increasing tip bias and is in good agreement with electron-electron scattering as derived from Fermi liquid theory with the addition of an elastic scattering term that is independent of tip bias. This provides insight into sources of both elastic and inelastic scattering of electrons in Cu.

References:

[1] Biqin Huang, et al., Phys. Rev. Lett. 99 177209 (2007)

[2] L. D. Bell and W. J. Kaiser, Phys. Rev. Lett. 61 2368 (1988)

[3]R. W. Soshea, et al., Phys. Rev. 138 A1182 (1965)

[4] J. M. Seiller, et al., Solid State Commun. 15 973 (1974)

[5]C. R. Crowell, et al., Phys. Rev. 127 2006 (1962)

11:00am **AS-WeM10 XPS Imaging Techniques for the Chemical Characterization of Fuel Cell Membrane Electrode Assemblies**, ***A.E. Wright****, T.S. Nunney, R.G. White,* Thermo Fisher Scientific, UK*, K.S. Reeves, K.L. More, H.M. Meyer III*, Oak Ridge National Laboratory

Fuel cell technology is reliant on the successful development of membrane electrode assemblies (MEA), which consist of a proton exchange membrane (PEM) sandwiched between catalyst-containing anode and cathode layers. X-ray photoelectron spectroscopy (XPS) with its high surface sensitivity and chemical state sensitivity is an ideal technique for characterizing fuel cell MEA chemical composition. Typically MEA membranes are in the range of 20-50μm thick, ruling out practical usage of conventional Ar ion or other profiling methods to obtain chemical composition profiles. To overcome these sample analysis constraints the MEA samples were prepared using an ultra low-angle microtomy (ULAM) technique. With the ULAM sectioning technique it is possible to extend a ~25 μm thick membrane to present an analysis area of over 400μm. Extending the analysis area of the MEA cross-section improves the opportunity to extract chemical state imaging information using a non-microscopy based technique such as XPS. Minimization of X-ray induced damage, preserving of chemical state information, is considered a significant experimental consideration for XPS polymer analysis. For this reason, rapid acquisition modes are preferred. This presentation will focus on the practicalities of rapid of XPS image acquisition methods and automated data review and processing techniques for the study of MEA structures

Research supported by the U.S. Dept. of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cell, and Infrastructure Technologies Program. Research at the ORNL SHaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Dept. of Energy.

11:20am **AS-WeM11 Formation of Hydroxyapatite Films on Thin Etridonate Films formed on Stainless Steel and Titanium Studied by Core and Valence Band XPS - A Potentially Biocompatible Surface for Implants**, *F. Gao,* ***P. Sherwood***, Oklahoma State University

This work reports the preparation of hydroxyapatite films formed on metals which were coated with a thin oxide free film of metal etidronate. The metals studied were stainless steel and titanium. The key to adhesion of the hydroxyapatite films is the initial formation of a thin, oxide free, etidronate film on the metal. It was not found possible to prepare the hydroxyapatite films directly on the metal surfaces. Since hydroxyapatite is a key component of bone and teeth, it is likely that the coated metals will have desirable biocompatible properties, and that these treated metals may find applications in the production of medical implants. The surface chemistry of the films was examined by core and valence band X-ray photoelectron spectroscopy. The valence band spectra were interpreted by cluster and band structure calculations. The valence band spectra proved especially valuable in the identification of the surface chemistry of the films.

11:40am **AS-WeM12 Enhancing Information Extracted from XPS Spectra using a Near Real-Time Data Analysis Package**, ***A.S. Lea****, K.R. Swanson, J.R. Haack, M.H. Engelhard, D.R. Sisk, D.R. Baer,* Pacific Northwest National Laboratory*, J.E. Castle,* University of Surrey, UK*, S. Tougaard*, University of Southern Denmark

The utilization of x-ray photoelectron spectroscopy (XPS) for the analysis of different types of materials is rapidly growing around the world due to the importance of surface and interfaces and the need for a more detailed analysis of many types of these materials. But, as the use of XPS expands, the knowledge of the technique by the typical user actually decreases and the knowledge and methods that have been developed over the years is not readily transferred to new users. To address this need, a method to automate some aspects of data analysis being developed in the Environmental Molecular Sciences Laboratory (EMSL) and is described here.

Real-time (or near real-time) analysis of the XPS data as it is collected has several potential advantages to scientists and instrument operators. It not only has the potential 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 and reporting, resulting in significant time (and cost) savings. The rapid data analysis can also impact the amount of data that needs to be collected and alter the course of planned measurements. Our development of a near real time XPS analysis has goals to provide atomic composition, carbon contamination layer thickness and component segregation (layer) information as soon as adequate data is collected on a specimen. This real-time data analysis package follows many elements of the expert system approach proposed by Castle[1] and some analysis methods developed by Tougaard[2]. A set of rules and algorithms are used to address a well defined series of analysis objectives to characterize the surface in terms of atomic concentration, layer sequences, and enrichment/depletion of elements as a function of depth.

We will demonstrate the rapid identification of the presence of carbon contamination (using an expert system approach to contrast this with carbon incorporation in the sample), production of a corrected surface composition analysis when the carbon is contamination, and determination of surface enrichment (or depletion) capabilities of our data analysis package using several examples of samples we have analyzed in our laboratory.

1. Castle, J.E., *J. Vac. Sci. Technol. A* 25(1) (2007) 1-27.

2. Tougaard, S., *J. Vac. Sci. Technol. A* 21(4) (2003) 1081-1086.

Biomaterial Interfaces
Room: K - Session BI+AS+BM+MS-WeM

Array-Based Sensors and Diagnostics: Grand Challenges
Moderator: D.W. Grainger, University of Utah, J. Shumaker-Parry, University of Utah

8:00am **BI+AS+BM+MS-WeM1 Design of Antibody Array-Based Sensors for Disease Proteomics: Grand Challenges**, ***C. Wingren***, Lund University, Sweden **INVITED**

Antibody-based microarray is a new proteomic methodology setting a novel standard for analysing complex, non-fractionated proteomes. The first generation of antibody micro- and nanoarrays has already demonstrated its potential for generating detailed protein expression profiles, or protein maps, of human body fluids in health and disease, paving the way for new discoveries within the field of disease proteomics. The process of designing highly miniaturized, high-density and high-performing antibody array set-ups have, however, proven to be challenging. In this presentation, the key technological challenges that must be resolved in a cross-disciplinary manner before true global proteome analysis can be performed using antibody array-based sensors will be presented and discussed.

In this context, we have successfully designed a set of state-of-the-art recombinant antibody array technology platforms for high-throughput proteomics. In more detail, we use human recombinant single-chain Fv (scFv) antibody fragments, microarray adapted by molecular design as probes, displaying an outstanding on-chip functionality and stability.

Uniquely, the platforms allows us to target both water-soluble as well as membrane proteins in a highly multiplexed and sensitive (pM to fM range) manner in complete, i.e. non-fractionated, directly labeled complex proteomes. Platforms compatible with a wide range of proteomes, including serum, plasma, urine, cell lysates, tissue extracts, intact cells etc, have been successfully designed. In addition, the first steps towards implementing label-free sensing (MS, MS -MS and SPRi) as well as designing self-addressable microarrays and miniaturized attovial-based nanoarrays as well as planar nanoarrays have been taken, clearly expanding the repertoire of technology platforms. The applicability of the platform(s) for differential high-content screening of clinical samples has been validated in a set of key applications within the field of oncoproteomics, autoimmunity, inflammatory diseases and allergy. The optimized antibody microarray technology platforms, as well as data from the screening analysis will be presented in context of the grand challenges the field experiences.

8:40am **BI+AS+BM+MS-WeM3 Development, Validation and Application of Q-Plex Array Technology**, ***M. Groll***, Quansys Biosciences Quansys Biosciences **INVITED**

The Quansys Q-Plex (multiplex ELISA) Array is a fully quantitative ELISA-based test where up to 25 distinct capture antibodies have been absorbed to each well of a 96-well plate in a defined array. This array is composed of 20 nanoliter spots with 350µm diameters and a pitch of 650µm between spots. Each spot represents a different distinct capture antibody population.

Using less than 30 µl of sample, up to 84 different samples can be assayed for all 25 unique analytes in less than 2.5 hours. Sensitivity is system dependent and typically ranges between 30 pg/ml to less than 1 pg/ml. All of the antibodies used in the Q-Plex arrays have been subject to a rigorous and comprehensive cross reactivity protocol and verified to be non-cross reactive with any other system on the array. Detection of this array is performed using the Quansys Q-View Imaging System. The image is then auto-processed using Quansys Q-View Software and concentrations for each analyte are output for the sample.

9:20am **BI+AS+BM+MS-WeM5 Drop on Demand Ink Jet Methods for Development and Manufacturing of Array Based Sensors and Diagnostics**, ***T.C. Tisone***, *A.V. Lemmo*, BioDot Inc.

The development and manufacturing of array based formats requires the transfer of biomarker reagents to a carrier substrate which forms the basis of a sensor for executing a multiplexed assay for research and diagnostics applications. The typical volume range for these types of assays is in the range of 100 pL up to 1000 nL: which lies in the range of commercial drop on demand piezoelectric and solenoid drop on demand dispensers. This presentation will discuss aspects of the physics and chemistry of successful applications of drop on demand methods to provide quantitative and high throughput reagent transfer to sensor substrates suitable for both Development and Manufacturing. Issues of drop formation, drop/substrate interactions and reagent/substrate interactions will be discussed. The agenda is to understand what role dispensing plays in the assay function.

10:40am **BI+AS+BM+MS-WeM9 New Molecular Strategies to Suppress Noise and Amplify Signal in Protein and DNA Microarrays**, ***A. Chilkoti***, Duke University **INVITED**

This talk will highlight recent work from my laboratory that addresses new interfacial technologies to suppress noise (N) and amplify signal (S) leading to heterogeneous assays with extraordinarily high S/N. In the first demonstration, I will focus on the adventitious adsorption of proteins as the primary factor that controls the limit-of-detection (LOD) of protein microarrays and limits the measurement of analytes from complex mixtures such as serum or blood. I will show data on a new protein microarray assay where background adsorption is effectively eliminated through the use of a protein-resistant –nonfouling– polymer brush. These “zero background” protein microarrays were successfully used to quantify protein analytes in serum with femtomolar LOD and a dynamic range of six orders of magnitude of analyte concentration. These LODs are 100-fold lower when compared to the same protein microarrays spotted on a conventional polymer substrate that displays high binding capacity but significant adventitious protein adsorption. This study also provided the first demonstration of the interrogation of an analyte directly from undiluted, whole blood by a protein microarray with a LOD of ~15 fM. Next, I will summarize recent work in my laboratory on the development of a new isothermal fluorescence signal amplification and detection scheme that exploits the ability of terminal deoxynucleotidyl transferase (TdTase) to add up to 100 fluorescent nucleotides to the end of a short DNA tag with an exposed 3’-OH. I will show how DNA microarrays that are printed on the nonfouling polymer brush exhibit low background signal, yet allow on-chip fluorescence signal amplification, leading to DNA microarrays that exhibit a sub-picomolar LOD, which appears to be the lowest LOD reported for DNA microarrays, to date.

11:20am **BI+AS+BM+MS-WeM11 SwitchDNA Biosensors for the Label-Free Detection and Sizing of Protein Targets on a Chip**, ***U. Rant***, *W. Kaiser, J. Knezevic, E. Pringsheim, M. Maruyama, P. Hampel*, Technische Universitaet Munich, Germany, *K. Arinaga*, Fujitsu Laboratories Ltd., Japan, *G. Abstreiter*, Technische Universitaet Munich, Germany

We introduce a chip-compatible scheme for the label-free detection of proteins in real-time that is based on the electrically driven conformation-switching of DNA oligonucleotides on metal surfaces. The switching behavior is a sensitive indicator for the specific recognition of IgG antibodies and antibody-fragments, which can be detected in quantities of less than 1 amol on the sensor surface. Moreover, we show how the dynamics of the induced molecular motion can be monitored by measuring the high-frequency switching response as well as by time-resolved fluorescence measurements. When proteins bind to the layer, the increase in hydrodynamic drag slows the switching dynamics, which allows us to determine the size of the captured proteins. We demonstrate the identification of different antibody fragments by means of their kinetic fingerprint. The switchDNA method represents a generic approach to simultaneously detect and size target molecules using a single analytical platform.

11:40am **BI+AS+BM+MS-WeM12 Nanomechanical Readout of DNA Microarrays**, *S. Husale*, Rowland Institute at Harvard University, ***H.H.J. Persson***, Stanford University, *O. Sahin*, Rowland Institute at Harvard University

DNA microarrays have enabled high throughput analysis of gene-expression and genotyping. However, they still suffer from limited dynamic range and rely heavily on enzymatic manipulations and amplification to create detectable signals. Here we present application of a novel nanomechanical detection method to microarray analysis that may circumvent these disadvantages. It is based upon a modified atomic force microscope (AFM) that can map mechanical properties of surfaces at high speed and spatial resolution. Mechanical measurements can reliably discriminate single and double stranded DNA on a surface. Automated image analysis reveals hybridized molecules with single molecule precision, thus providing a digital measure of hybridization. This method can detect a broad range of target concentrations with a limit of detection in the low attomolar concentration range without any labeling, enzymatic manipulations, and amplification. We demonstrate the performance of this technique by measuring differential expressions of miRNAs in tumor samples, which has been shown to help discriminate tissue origins of metastatic tumors.

Electronic Materials and Processing
Room: B1 - Session EM-WeM

Organic & Molecular Electronics
Moderator: L.M. Porter, Carnegie Mellon University

8:00am **EM-WeM1 Nanoscale Guided Molecular Engineering of Organic Electro-Optical Materials**, ***D.B. Knorr***, *X. Zhou, Z. Shi, J. Luo, S. Jang, A.K.-Y. Jen, R.M. Overney*, University of Washington

Increasing complexity in bottom-up molecular designs of amorphous structures with multiple relaxation modes demand an integrated and cognitive design approach, where chemical synthesis is guided by both analytical tools and theoretical simulations. This is true of organic second-order nonlinear optical (NLO) materials, which are being actively pursued for applications in photonic devices. For practical applications, NLO materials must have both high macroscopic EO activity and thermal stability. High EO activity can be achieved by acentrically ordering a system containing a high density of high dipole chromophores via electric field poling at elevated temperatures. Thermal stability requires the system to have internal constraints to prevent collapse of the acentric order at operating temperatures. Recent efforts for achieving both requirements have focused on dendrons capable of self-assembly through arene-perfluoroarene (Ar^H-Ar^F) quadrupolar interactions within self-assembled glassy chromophore systems, which provided excellent EO activity above 300pm/V and good thermal stability.

In this study, nanoscale scanning probe based thermo-mechanical analyses, intrinsic friction microscopy (IFM) and shear-modulation force microscopy yield direct insight into the molecular enthalpic and entropic relaxation modes of these materials. Ar^H-Ar^F interactions of dendritic moieties for coarse self assembly are found to impose three phase relaxation regimes with two transition temperatures, T_1 and T_2. Energetic analyses based on IFM identify increasing temporal stability with increasing arene size for the low temperature regime. Electric field poling efficiency is found to be inversely proportional to entropic cooperative contributions. Based on a molecular dynamic simulation, activation energies are tied primarily to interactions between chromophore (dipole), dendritic (quadrupole) moieties and combinations thereof below the incipient glass transition temperature. Above T_1, molecular mobility becomes increasingly cooperative. Sufficient mobility exists in the region of $T_1<T<T_2$ to allow for chromophore acentric electric field alignment, as non-covalent interactions associated with stabilization of the system below T_1 are in competition with melt-like effects. Further, cooperativity increases with increasing arene size, and accounts for approximately 80% of the observed apparent activation energy above T_2. Although beneficial to temporal stability with increased operating temperatures, cooperativity was found to lower the poling efficiency. Future synthesis efforts therefore must balance cooperativity to obtain satisfactory results in both stability and efficiency.

8:20am **EM-WeM2 Perpendicular Interaction between Donor and Accepter Molecules on Au(111) Surface**, ***U.G.E. Perera***, Ohio University, *R. Mishima,* Osaka University, Japan, *S.-W. Hla*, Ohio University

When two types of molecules having opposite tendency to donate and accept electrons are put together, charge transfer between the molecules can take place. Charge transfer alters the frontier molecular orbitals, and thus it can be used to engineer materials having a wide range of properties. Investigation of the charge transfer processes at a molecular level is a new avenue of exciting research. Here, we present a low temperature scanning tunneling microscopy (STM) and spectroscopy study of single molecule level charge transfer process between decamethylmanganocene (Mn(C5Me5) 2) and 7,7,8,8- tetracyanoquinodimethane (TCNQ) on a Au(111) surface at 4.6K. Both molecules are deposited onto an atomically clean Au (111) surface at an ultrahigh vacuum environment. On Au(111), the TCNQ molecules form well ordered two dimensional self-assembled clusters while the Mn(C5Me5)2 molecules adsorb either on TCNQ layer or on the bare surface areas. The STM images show that Mn(C5Me5)2 molecules position on the surface with tilted cyclopentacene rings. A comparative tunneling spectroscopy between the Mn(C5Me5)2 /Au(111) and Mn(C5Me5)2/TCNQ/Au(111) assemblies clearly reveals the shift of frontier molecular orbitals and thus the detailed charge transfer mechanism induced by deposition of Mn(C5Me5)2 has been able to explain. This research is supported by the United States Department of Energy BES grant number DE-FG02-02ER46012.

8:40am **EM-WeM3 An Ultra-Thin Molecular Superconductor**, *K. Clark,* Ohio University, *A. Hassanien,* Nanotechnology Research Institute, Japan, *K.-F. Braun,* Physikalisch Technische Bundesanstalt, Germany, *H. Tanaka,* Nanotechnology Research Institute, Japan, ***S.-W. Hla***, Ohio University

Almost a century after its discovery by H. Kamerlingh Onnes, superconductivity continues to be an inspirational subject for many physicists because of its rich physical phenomena. Among a variety of superconducting materials, the organic superconductors are regarded as “unconventional superconductors” based on the different nature of their superconducting states as compared to the conventional BCS superconductors. A class of Bechgaard type5 charge transfer salts having a D_2A arrangement, where D and A are the donor and acceptor respectively, exhibit superconductivity in the bulk. Here, we form an ultra-thin Bechgaard salt with the smallest possible molecular-unit thickness composed of just a sheet of molecular layer having individual $GaCl_4$ molecules sandwiched between the chains of a double domino stacked BETS on a Ag(111) surface. Remarkably, scanning tunneling spectroscopy of this ultra-thin Bechgaard layer at 5.4K reveals a clear superconducting gap exhibiting d-wave pairing symmetry. Real space spectroscopic images with a molecular resolution provide an experimental paradigm: The stacked BETS chains in the layer act as the superconducting sites. In stark contrast to the high T_c superconductors, the spectroscopic maps clearly display nanoscale electronic order indicating a robust superconductivity down to an extreme spatial limit.

9:00am **EM-WeM4 Correlating Structure and Electronic Properties in Oligothiophene Monolayers, an AFM Study**, ***F. Martin***, *B. Hendriksen, A.J. Katan,* Lawrence Berkeley National Laboratory, *C. Mauldin,* University of California, Berkeley, *J.M.J. Frechet, M. Salmeron*, Lawrence Berkeley National Laboratory

Organic compounds are currently considered as the main building block of electronic devices that could lead to new commercial applications which include flexible electronics as well as organic photovoltaics. Correlating structural and electrical properties is a key requirement to understand charge transport in organic thin films.

We investigated the effect of crystallinity and grain boundaries on the conductivity of Langmuir-Blodgett oligothiophene monolayers using Current-Sensing Atomic Force Microscopy (CS-AFM).

We used the AFM tip as a tool to inject charges and manipulate the crystalline monolayer. We found that passing electrical current locally from the conductive AFM tip led to reversible charging of the native SiO2 layer supporting the film as far as microns away from the charge injection point. This effect, due to charge spreading through the crystalline monolayer, was used to image conduction pathways and study the effect of grain boundaries on the resistivity of the monolayer.

In addition, we found that scanning manipulation at loads in the order of 100nN lead to a 5 fold decrease of the monolayer conductivity in CS-AFM. Subsequent molecular resolution AFM revealed that the degree of crystalline order in manipulated regions of the monolayer had strongly decreased, offering a direct proof of the correlation between order and conductivity in organic monolayers.

9:20am **EM-WeM5 Transport through a Single Octanethiol Molecule Adsorbed on a Pt-modified Ge(001) Surface**, ***D. Kockmann***, *H.J.W. Zandvliet, B. Poelsema*, University of Twente, Netherlands

We have studied (single) octanethiol molecules adsorbed on a Pt-modified Ge(001) surface, using scanning tunneling microscopy/spectroscopy.

On a clean Ge(001) surface we deposited a submonolayer amount of platinum by evaporation. Patches of dimerized atomic chains form via self-organization on the surface during the subsequent annealing-step. We have decorated the Pt-modified Ge(001) surface with octanethiol molecules. STM at 77 K revealed that at low coverage the molecules selectively adsorb on the Pt chains and not on the underlying terrace. The molecules lay down on the Pt chains, in contrast to SAM's, where they stand upwards.

In order to distinguish between the octane-tail and the thiol-head of the molecule, we have performed STS above the different regions of the molecule, again at 77 K. We observed that the I(V) spectra recorded above the thiol-head were conspicuously different from the spectra recorded above the octane-tail. From that we could determine the molecular orientation of the adsorbent.

In addition, we have measured current-time traces on the adsorbed octanethiol molecules. Throughout these experiments we turned off the feedback-loop of the STM. Then each measurable rearrangement or conformational change of the molecule is reflected in the I(t) traces. During these measurements we occasionally found a sudden dramatic increase in current from 1 nA (set point current) to values between 10-15 nA. The residence times at this high current varied between 10-40 seconds. In most cases the current jumps back to its original set point value of 1 nA within the open-loop measurements, which typically last for 50-100 seconds. STM images recorded after the open-loop experiments revealed that the octanethiol molecules remained at their original position.

From these observations we concluded that during the I(t) measurements the molecule wagged its tail upward, thereby making contact with the tip of the STM. Hence, we measured electron transport through the molecule instead of electron tunneling from tip to molecule. The derived single molecule resistance, 100-150 MΩ, is in accordance with literature.

9:40am **EM-WeM6 Modulation of Charge Injection and Transport in Poly(3-hexylthiophene)-Based Field-Effect Transistors by Self-Assembled Monolayers**, ***K.A. Singh***, *T. Nelson, J. Belot, R.D. McCullough, T. Young, T. Kowalewski,* Carnegie Mellon University, *P. Nachimuthu, S. Thevuthasan,* Pacific Northwest National Laboratory, *L.M. Porter*, Carnegie Mellon University

Charge injection and transport in bottom-contact poly(3-hexylthiophene) (P3HT) based field-effect transistors (FETs), wherein the Au source and drain contacts are modified by self-assembled monolayers (SAMs), is reported. Four SAMs of different chemical composition were selected to either enhance or reduce charge injection across the contacts. The rr-P3HT films were drop cast from a solution in chloroform in a saturated environment. Prior to P3HT deposition the FETs were treated with octyltrichlorosilane (OTS) solution in hexadecane for 2 hrs, dried and then immersed in a solution containing one of the SAMs in ethanol for another 2 hrs. The contact resistance (R_C) was measured using the transmission line method and the effective field-effect mobility (μ) was determined from the linear region of the transistor characteristics. Treatment of FETs with the first two SAMs resulted in an increase in μ and a decrease in R_C, whereas treatment with the other two SAMs resulted in a decrease in μ and an increase in R_C. For example, in one case, μ increased from 0.15 to 0.20 $cm^2V^{-1}s^{-1}$ and R_C decreased from 0.61 to 0.34 MΩ; in the opposite case, μ decreased to 0.09 $cm^2V^{-1}s^{-1}$ and R_C increased to 0.90 MΩ. The electrical properties of the transistors correlate with changes in the metal workfunction by up to 0.9 eV, as estimated using ultraviolet photoelectron spectroscopy. Besides using the SAMs for tuning the charge injection, the monolayer formed by OTS on SiO_2 at the insulator/ P3HT interface resulted in improved morphology of the P3HT film, as observed by atomic force microscopy, and an associated increase of μ from 0.03 to 0.15 $cm^2V^{-1}s^{-1}$. In summary, the charge carrier injection and transport in P3HT-based FETs were successfully modulated by treatment with SAMs. The use of OTS at the SiO_2/P3HT interface also resulted in improved morphology and enhanced charge transport. Further details regarding the use of self-assembled monolayers will be presented along with the device and photoemission characteristics.

10:40am **EM-WeM9 Reliable and Selective Formation of Metallic Contacts to Organic Thin Films: Towards Molecular Electronics**, *P. Lu, Z. Shi, **A.V. Walker***, Washington University in St. Louis

We have investigated the selective deposition of copper on alkanethiolate self-assembled monolayers (SAMs) using electroless deposition. This work has important applications in molecular and organic electronics, sensing, biotechnology, photonics and other technologies. We demonstrate that useful deposition rates can be obtained by "self-seeding" - the immersion of the SAM in a solution containing Cu^{2+} ions prior to addition of the reducing agent, formaldehyde. The selectivity of the deposition is achieved by *increasing* the bath temperature to 45 ºC. At this temperature Cu deposition ceases on $–CH_3$ terminated SAMs but continues on –COOH terminated SAMs. Finally, and perhaps most importantly, copper penetration through SAMs can be prevented by the addition of adenine to the bath. The addition of adenine also leads to smooth film morphologies. Each of these effects is explained by the formation of complexes with the SAM terminal group. Copper-terminal group complexes lead to useful deposition rates and control of the selectivity of the deposition. The formation of adenine-terminal group complexes prevents Cu penetration through the monolayer. Similarly, we observe that strongly adherent nickel films can be selectively deposited on functionalized SAMs through careful control of the bath conditions, especially temperature and pH.

11:00am **EM-WeM10 Quantum Dot Polymer Light Emitting Device With a Zinc Oxide Nanoparticle Film**, ***L. Qian**, Y. Zheng, J. Xue, P.H. Holloway*, University of Florida

A polymer light emitting device (PLED) with an active layer consisting of CdSe/ZnS or CdS/ZnS core/shell quantum dots (QDs), and an electron transport/passivation layer consisting of 5 nm ZnO nanoparticles has been studied. The complete device consists of a glass substrate with the following layers: glass/ITO/PEDOT-PSS/poly-TPD/QDs/ZnO/Al-top-contact. The PEDOT-PSS, poly-TPD, QD, and ZnO layers were all deposited from solutions using spin casting, while the ITO layer was sputter deposited and the Al contact was deposited by thermal evaporation through a shadow mask. Thus the device is predominantly a solution-processed QD-PLED with simple vacuum processing instead of thermal evaporation of multiple organic small molecule layers. The emitted color was tuned from blue (CdS/ZnS) to green or red (CdSe/ZnS) by adjusting the composition and size of the QDs. Use of the ZnO layer reduced the injection voltage for a brightness of ~200 cd/m^2 from ~11 to ~2.6 V (green light), and improved the stability with time. For example, an unencapsulated QD-PLED with a ZnO nanoparticle layer exhibited a stable ~200 cd/m^2 brightness for 18 hrs in ambient air, while a comparable device without the ZnO layer degraded from 80 to 6 cd/m^2 in 3 hrs under the same conditions. The reasons for these improvements will be discussed.

11:20am **EM-WeM11 Effects of Different Organic Passivation Layers on the Electrical Stabilities of Flexible Organic Thin Film Transistors under Cyclic Bendin**, ***Y.G. Seol**, J.S. Park, J.H. Ahn, N.-E. Lee*, Sungkyunkwan University, Korea

One of the critical issues for applications of flexible organic thin film transistors (OTFTs) for flexible electronic systems is the electrical stabilities of the OTFT devices, including variation of the current on/off ratio (I_{on}/I_{off}), leakage current, threshold voltage, and hysteresis, under repetitive mechanical deformation. In particular, repetitive mechanical deformation accelerates the degradation of device performance at the ambient environment. In this work, electrical stabilities of the pentacene organic thin film transistors (OTFTs) employing various passivation layers were investigated under mechanical cyclic bending. Flexible bottom-gated pentacene-based OTFTs fabricated on flexible polyimide substrate with poly-4-vinyl phenol (PVP) dielectric as a gate dielectric were passivated by the solution-processed, evaporated, and plasma-deposited organic layers. For cyclic bending experiment of flexible OTFTs, the devices were cyclically bent up to 10^5 times with 5 mm bending radius. In the most of the devices after 10^5 times of bending cycles, the off-current of the OTFT with no passivation layers was quickly increased due to increases in the conductivity of the pentacene caused by doping effects from O_2 and H_2O in the atmosphere, which leads to decrease in the I_{on}/I_{off} and increase in the hysteresis. With passivation layers, however, the electrical stabilities of the OTFTs were improved significantly. In particular, the OTFTs with plasma-deposited organic layers showed the best electrical stabilities up to the bending cycles of 10^5 times compared to the devices with the solution-processed or thermal-evaporated organic layer. Changes in electrical properties of cyclically bent OTFTs with different organic passivation layers will be compared and discussed in detail.

Energy Frontiers Research Centers
Room: A8 - Session EN-WeM

Energy Frontiers Research Centers
Moderator: E.S. Aydil, University of Minnesota

10:40am **EN-WeM9 EFRC: Science of Precision Multifunctional Nanostructures for Electrical Energy Storage**, ***G.W. Rubloff***, University of Maryland **INVITED**

Current technology for electrical energy storage (EES) imposes profound limits on needed advances in energy capture, its efficient utilization, and its impact on the environment. Renewable sources with time-varying output (e.g. solar, wind) require storage mechanisms, while electric vehicles with environmental as well as energy benefits need better storage mechanisms to enable longer distances and faster recharge than expected commercially in the short term. Our EFRC is aimed at providing the scientific underpinnings for a new generation of nanostructure solutions to enable EES devices with dramatic improvements in power (10-100X) and energy density (10X). We believe such advances are possible by suitable design of heterogeneous nanostructures that provide facile, repeatable and bidirectional transport of ions and electrons between high capacity nanostructures (e.g. nanowires) and remote contacts to the external world, while stabilizing efficient charge storage components during charge cycling. Multifunctional nanostructures will be investigated which combine efficient charge storage materials (metal oxides, Si) with low-dimensional carbon for accelerated charge transport to storage nanostructures and mechanical robustness during cycling, with focus synthesis in precise, well-controlled configurations as needed in massive arrays. Fundamental electrochemistry at the nanoscale will be explored experimentally and theoretically, enhanced by the development of new MEMS instruments for nanoscale in-situ observations of electrochemical phenomena and structural change during charge cycling. The EFRC is led by the University of Maryland in partnership with Sandia and Los Alamos National Laboratories, the University of California Irvine, the University of Florida, and Yale University. The effort benefits from research facilities and infrastructure of the Maryland NanoCenter, University of Maryland Energy Research Center, and the Center for Integrated Nanotechnologies at Sandia and Los Alamos.

11:20am **EN-WeM11 Research at the Center on Materials for Energy Efficiency Applications (CMEEA)**, ***J.E. Bowers***, University of California Santa Barbara **INVITED**

As a result of the energy crisis facing the United States, the scientific enterprise must offer solutions, based on fundamental research and engineering, that will ensure sustainable energy resources for the US over the long term. The Center on Materials for Energy Efficiency Applications (CMEEA) addresses this critical challenge by focusing on fundamental research in the three key areas of photovoltaics, thermoelectrics, and solid state lighting. CMEEA is composed of 22 senior scientists and additional graduate and undergraduate students at UCSB, NREL, LANL, UCSC and Harvard. CMEEA will take a comprehensive, integrated approach to dramatic improvement in photovoltaic technology, anticipating lower cost manufacturability with organic solar cells, higher performance epitaxial photovoltaics for concentrated PV and truly novel materials and device structures in the longer timeframe that will address both higher efficiency and lower cost. New thermoelectric materials with higher efficiencies are critically important for power generation and waste heat recovery. Material breakthroughs would allow a variety of new applications, such as an attractive compact alternative to internal combustion engines and solid state refrigerators. We are proposing a variety of metal/semiconductor nanocomposites that will allow us to modify the three intrinsic material properties important for high efficiency. Research in solid-state lighting will focus on the dramatic drop in efficiency in the yellow-green region by using nonpolar materials to reduce leakage due to the QCSE and due to the Auger effect.

Exhibitor Workshops
Room: Exhibit Hall 1 - Session EW-WeM

Exhibitor Workshop
Moderator: R.A. Langley, Consultant

10:20am **EW-WeM8 RJ Lee Group's Advanced FESEM/STEM and XPS Analytical Services for Exploring the Nano-World**, ***B.R. Strohmeier***, *K.L. Bunker, J.D. Piasecki*, RJ Lee Group, Inc.

RJ Lee Group, Inc. (RJLG, www.rjlg.com) is an organization of experts who provide the highest quality microscopy, analytical, and consulting services to our clients and partners. Leading organizations come to RJLG for more than data and information; they come for an innovative approach and technical solutions developed through our commitment to quality, reliability, and customer satisfaction. RJLG is presently the exclusive commercial analytical testing laboratory in the United States to offer analytical services with: 1) the Hitachi S-5500 electron microscope, which combines field emission scanning electron microscopy (FESEM) and low kV scanning transmission electron microscopy (STEM) with energy dispersive X-ray spectroscopy (EDS) and 2) the Thermo Fisher Scientific K-Alpha X-ray photoelectron spectroscopy (XPS) instrument. The S-5500 and K-Alpha are two of the most powerful materials and surface characterization instruments available to scientists today. This presentation will give a brief overview of the advanced capabilities of each instrument along with examples of applications of these instruments for the characterization of nanomaterials.

The highlight of the Hitachi S-5500 electron microscope is the cold field emission electron source and the in-lens technology, which together achieve the world's highest secondary electron imaging resolution of 0.4 nm at 30 kV. The electron optical design of the Hitachi S-5500 places the sample at the optimum analytical and imaging working distance, allowing concurrent acquisition of high-resolution FESEM and STEM images, as well as EDS information. A variety of signals can be collected simultaneously including secondary electron and backscattered electron FESEM images and bright field (BF) and dark field (DF) STEM images. Combining this instrument with new silicon drift detector (SDD) technology (Bruker 30 mm^2) allows for high resolution elemental analysis and mapping of nanostructures. Therefore, the S-5500 can obtain unique information on samples that single standard microscopy techniques, such as SEM and TEM, are not able to accomplish when used alone.

XPS is a highly surface-sensitive and quantitative technique for materials characterization. The Thermo Fisher Scientific Model K-Alpha XPS is a compact, fully integrated, state-of-the-art instrument, with many outstanding features such as: 1) a high intensity, monochromatic, Al Kα X-ray source with an analytical spot size that can be easily varied from 30-400 µm, 2) a high transmission, high spectral resolution, electron energy analyzer, 3) a high sensitivity multi-channel detector, 4) a versatile sample stage capable of handling large or multiple samples with various sample mounting options, 5) *in situ* optical sample viewing and positioning, 6) elemental and chemical state surface mapping capability, 7) high quality depth profiling performance, 8) an unprecedented, highly automated, operation intended for non-expert and multi-user environments, and 8) advanced data processing software. Nanometer scale sampling depth and its ability to provide chemical state information makes XPS an ideal analytical technique for investigating the elemental and chemical surface composition of nanoparticles and other complex advanced materials.

Graphene Topical Conference
Room: C3 - Session GR+MI-WeM

Spins in Graphene: Injection and Manipulation
Moderator: O.M.J. van 't Erve, Naval Research Laboratory

8:20am **GR+MI-WeM2 Graphene Extraordinary Magnetoresistive Devices**, ***S. Pisana***, *P.M. Braganca,* Hitachi GST, *M. Pelliccione,* Stanford University, *M. Nishioka, N. Smith, E.E. Marinero, B.A. Gurney*, Hitachi GST

Extraordinary magnetoresistance (EMR) has recently attracted interest for magnetic field sensing applications in the magnetic storage industry [1]. The effect is particularly attractive given the magnitude of its response, which is comparable to current giant magnetoresistive sensors for mesoscopic device sizes, and its lack of thermal magnetic noise, as the structure does not incorporate ferromagnetic materials. EMR devices consist of hybrid semiconductor-metal structures in which the exclusion of current from a metal shunt in a magnetic field modulates the resistance of the device. This functionality can be advantageously combined with the Hall effect with appropriate variations in the device's lead configuration [2].

The EMR response is proportional to the semiconductor's mobility, among other factors. Furthermore, the successful implementation of this type of device for future read sensors in magnetic storage applications restricts the sensing element's position within a few nanometers from the source of magnetic field.

Graphene, a single atom-thick layer of graphite, is a promising electronic material, given its high mobility, high current carrying capabilities and linearly dispersive electronic bands [3]. These qualities make it a promising candidate for magnetic field sensing in an EMR device, allowing for the conceptually smallest magnetic spacing in a structure that is free from thermal magnetic noise.

In this work, we outline the first implementation of graphene EMR devices. We will discuss their mesoscopic fabrication and demonstrate response that is comparable to current magnetic field sensors. Devices with minimum feature of 150 nm (Figure 1) show signals above 2 mV in magnetic fields of 350 Oe at room temperature. The results are summarized in the context of future magnetic field sensors for terabit density data storage.

[1] Solin, S. A.; Thio, T.; Hines, D. R. & Heremans, J. J.; Science **289**, 1530 (2000)

[2] Boone, T. D.; Smith, N.; Folks, L.; Katine, J. A.; Marinero, E. E. & Gurney, B. A.; IEEE Electron Device Letters **30**, 117 (2009)

[3] Geim, A. K. & Novoselov, K. S.; Nature Materials **6**, 183 (2007)

8:40am **GR+MI-WeM3 Electronic Spin Transport and Spin Precession in Single Graphene Layers at Room Temperature**, *B.J. van Wees,* ***N. Tombros***, University of Groningen, the Netherlands **INVITED**

I will give an overview of electron spin injection, spin transport, spin precession and spin manipulation in graphene. The focus will be on recent experiments on single graphene field effect devices with ferromagnetic contacts. The use of the so-called non-local geometry allows a detailed investigation of various aspects of spin injection and spin transport.

I will first give a basic introduction into the "standard model" for spin transport and show how it can be applied to carbon systems, in particular graphene. The Bloch equations will be explained, which describe the processes of spin diffusion, drift, precession and relaxation. Following that will discuss that:

a) Spins can be transported through a graphene layer with a spin relaxation length of about 1.5 micrometer. By applying a perpendicular magnetic field Hanle spin precession can be studied and information about spin relaxation and the carrier diffusion can be obtained [1].

b) By applying a large DC electric field the transport of spins between injector and detector can be manipulated (sped up or slowed down) using carrier drift [2].

c) The spin relaxation is found to be slightly anisotropic, with spins directed perpendicular to the graphene plane relaxing faster than spins directed in the plane [3].

d) Spins can be injected into graphene with an injection efficiency up to 20 percent. This injection efficiency can be enhanced by a current bias which takes the carriers away from the injecting contacts. In this way injection efficiencies up to 38% have been achieved [4].

e) We have observed a scaling between the spin relaxation times and lengths and the carrier mobility in graphene [5,6]. I will discuss the possibility that in intrinsic graphene (where the carriers are only scattered by electron-phonon interaction) spin relaxation lenghts of 100 micrometer in graphene at room temperature might be possible, and even longer ones at lower temperatures. Related to that I will discuss the potential of graphene for future spintronics applications.

[1] N. Tombros et al., Nature 448, 571 (2007)

[2] N. Tombros et al., Phys. Rev. Lett. 101, 046601 (2008)

[3] C. Jozsa et al., Phys. Rev. Lett. 100, 236603 (2008)

[4] C. Jozsa et al., Phys. Rev. B 79, 081402 R (2009)

[5] M. Popinciuc et al., submitted to Phys. Rev. B.

[6] C. Jozsa et al, in preparation.

9:20am **GR+MI-WeM5 Quantum Hall Effect in Suspended Graphene Devices**, ***S.Y. Jung***, *N.N. Klimov,* NIST and University of Maryland, College Park*, J.A. Stroscio, D.B. Newell, N.B. Zhitenev*, National Institute of Standards and Technology

High carrier mobility and long coherence lengths are one of the main attributes which have attracted so much attention to graphene as a new electronic material. Recent studies have shown that the mobility in graphene is extremely sensitive to disorder, particularly coming from substrate interactions [1]. Substrate interactions can be minimized or possibility eliminated by fabricating suspended graphene devices [2]. In this presentation, we present results where we systematically study the quantum Hall effect in suspended graphene devices varying device geometry and disorder. Suspended graphene devices allow for a broad range of particular realizations of the disorder potential. Magnetotransport properties are investigated at various temperatures and with respect to the influence of current annealing. Device geometries with two- and four-probe terminals and different aspect ratios are compared and the effects of disorder potential modifications are discussed.

[1]. J. Martin et al, Nature Phys. **4**, 144 (2008).

[2]. K. I. Bolotin et al, Phys. Rev. Lett. **101**, 096802 (2008).

9:40am **GR+MI-WeM6 Spin Injection and Transport in Single Layer Graphene**, ***W. Han****, *K. Pi, K. McCreary, W. Bao, C.N. Lau, R. Kawakami*, University of California, Riverside

Single-layer graphene (SLG) is an attractive material for spintronics due to its tunable carrier concentration and polarity, weak spin-orbit coupling, its quasi-relativistic band structure with symmetric electron and hole bands. We fabricated the SLG spin valves using transparent Co/SLG contacts and studied the spin dependent properties by non-local magnetoresistance (MR) measurements at room temperature. Hanle effect confirms that the non-local signal originates from spin injection and transport and gives a spin relaxation time of ~84 ps and a spin diffusion length of ~1.5 µm. Spacing dependence of the non-local MR indicates a spin diffusion length of ~1.6 µm and a spin injection/detection efficiency of 0.43. Gate voltage dependence shows that the non-local MR is proportional to the conductivity of the SLG, which is the predicted behavior for transparent ferromagnetic/nonmagnetic contacts. Bias dependence of the non-local MR reveal an electron-hole asymmetry in which the non-local MR is roughly independent of bias for electrons, but varies significantly with bias for holes.

10:40am **GR+MI-WeM9 Spin Polarized Electrons in Graphene Nanoribbons**, ***Y.-W. Son***, Korea Institute for Advanced Study, Korea **INVITED**

In this talk, I will discuss the electronic and magnetic properties of graphene nanoribbons with homogeneous edge structures. Several calculation methods including self-energy corrections and/or strong Coulomb interactions are introduced to study magnetic orderings and their robustness along the zigzag shaped edges on both sides of graphene nanoribbons. I will also discuss special interplays between external electric fields and magnetic orderings in graphene nanoribbons and a possible realization of half-metallic phase in conventional experimental setups with various substrates or molecular adsorptions.

11:40am **GR+MI-WeM12 Observation of Charge Puddles and Edge Effect in a Graphene Device by Scanning Gate Microscope**, ***J.S. Chae***, Seoul National University, Korea, *S.Y. Jung, N.B. Zhitenev, J.A. Stroscio,* National Institute of Standards and Technology, *Y. Kuk*, Seoul National University, Korea

Despite the recent progress in understanding the geometric structure of defects and edge atoms and their role in the transport property in a graphene sheet, there has been no report showing direct correlation between them. That is because the structural studies were performed using microscopic tools such as scanning tunneling microscopy and other electron microscopies, while the transport property measurement was done macroscopically in a two or four terminal device with a back gate. Scanning Gate Microscope (SGM) is a unique microscopic tool with which the local electronic structure and the transport property of a device can be measured simultaneously. A SGM uses a conducting tip to apply an electric field locally and measures the transport current through two or four contacts and utilizes the same tip to measure the geometric structure in Atomic Force Microscopy (AFM) mode. In this experiment, we observed a conductance change originated from the spatial distribution of charge puddles with a length scale of ~ 100nm in a graphene device, very similar to the previously reported results1) measured with AFM with a single electron transistor tip. We discovered that the charge puddles can be detected only when the local Fermi level of a gated area by the tip bias is near the Dirac point. We also discovered that there is strong conductance enhancement when the tip is placed along the edges of a graphene device. We think that this edge effect can be explained by the fact that there is a strong charge accumulation at the edges in a charged graphene2)

1) J. Martin, N. Akerman, G. Ulbricht, T. Lohmann, J. H. Smet, K. von Klitzing & A. Yacoby, Nature Physics, **4**, 144 (2008)

2) P.G. Silvestrov and K.B. Efetov, Phys. Rev. B **77**, 155436(2008)

---

* Falicov Student Award Finalist

Inkjet Technology: Printing, Materials Processing, and Microfluidics Fundamentals Topical Conference
Room: B3 - Session IJ+BI+MN-WeM

Microfluidic Fundamentals and Inkjet Technology
Moderator: G.E. Mårtensson, Mydata Automation AB

8:00am **IJ+BI+MN-WeM1 The Life and Death of a Drop: Topological Transitions and Singularities in Fluids**, *S. Nagel*, ***N.C. Keim***, University of Chicago **INVITED**

The exhilarating spray from waves crashing into the shore, the distressing sound of a faucet leaking in the night, and the indispensable role of bubbles dissolving gas into the oceans are but a few examples of the ubiquitous presence and profound importance of drop formation and splashing in our lives. They are also examples of a liquid changing its topology. Although part of our common everyday experience, these transitions are far from understood and reveal delightful and profound surprises upon careful investigation. For example in droplet fission, the fluid forms a neck that becomes vanishingly thin at the point of breakup. This topological transition is thus accompanied by a dynamic singularity in which physical properties such as pressure diverge. Singularities of this sort often organize the overall dynamical evolution of nonlinear systems. I will first discuss the role of singularities in the breakup of drops. I will then discuss the fate of the drop when it falls and eventually splashes against a solid surface.

8:40am **IJ+BI+MN-WeM3 Liquid Fragmentation**, ***E. Villermaux***, Marseille Universite, France **INVITED**

Fragmentation phenomena will be reviewed with a particular emphasis on processes occurring with liquids, those giving rise to drops --in the broad sense, the process of atomization--. Various observations converge to propose a unifying scenario describing the overall transition between a compact macroscopic liquid volume and its subsequent dispersion into stable drops. In liquids, primary instabilities always give birth to more or less corrugated ligaments whose breakup induce the shape of the drop size distribution in the resulting spray. Examples include the fragmentation of jets and liquid sheets, the formation of spume by the wind blowing over a liquid surface, bursting phenomena, impacts and raindrops.

9:20am **IJ+BI+MN-WeM5 Dripping and Jetting: Mechanisms of Droplet Formation in Two- and Three-Phase Flows**, *A.S. Utada,* Harvard University and University of Tokyo, Japan, ***A. Fernandez-Nieves,*** Georgia Institute of Technology, *D.A. Weitz*, Harvard University **INVITED**

Drop formation is an ubiquitous process familiar from our daily life. For example, water flowing through a faucet will break into droplets through one of two different mechanisms: discrete droplets will drip from the tap at low flow rates or a continuous jet will flow from the tap at higher flow rates. A qualitatively similar process happens when drop formation occurs within a second immiscible liquid. However, in this case, the presence of surface tension between the two immiscible liquids fundamentally alters the dynamics. We describe the transition between dripping and jetting in a coflowing stream within a microfluidic device and show that this transition can be understood with a general phase diagram [1]. Building on this understanding, we use a modified microfluidic device to generate monodisperse double emulsions from which we use to form novel core-shell structures [2].

[1] A. S. Utada, A. Fernandez-Nieves, H. A. Stone, D. A. Weitz, Phys Rev Lett **99**, 094502 (2007).

[2] A. S. Utada *et al*., Science **308**, 537 (2005).

10:40am **IJ+BI+MN-WeM9 Interplay between Simulation, Theory, and Experiment in Nonstandard Inkjet Printing: From New Devices to Complex Fluids**, ***O.A. Basaran***, Purdue University **INVITED**

During its early days, applications of inkjet printing were restricted almost exclusively to the graphic arts. In the late 1990s, the method found widespread application in DNA arraying. More recently, the applications of inkjet technology have broadened considerably to span areas as diverse as direct printing of electronic circuits and solar cells and drop-by-drop construction of organs and other biological structures. Inkjet printing involves the formation of drops from nozzles and the subsequent impact and deposition of such drops on suitable substrates. Both drop formation and drop impact are prototypical free surface or free boundary problems involving large deformation and breakup of fluid-fluid interfaces. Given the ever decreasing time and length scales inherent to inkjet printing, e.g. micron size drops are formed from an inkjet nozzle in time scales of microseconds, and that inkjet printing is a free boundary problem that involves finite time hydrodynamic singularities, e.g. pressures and velocities blow up in finite time as the drop surface approaches breakup or pinch-off, simulation, theoretical description, and experimental visualization of the dynamics of inkjet drops are challenges to the modeler, the theorist, and the experimentalist alike. Moreover, many of the emerging applications of inkjet printing involve fluids that can be characterized as complex fluids in that their bulk rheologies are non-Newtonian and/or their surface tensions vary in time. Motivated by research being carried out in the PI's group on inkjet printing of drops of complex fluids containing pharmaceutical active ingredients on edible substrates, this talk will focus on how computation, theory, and experiment are being used in concert to advance the state-of-the art in the field. Examples that will be used to highlight the computations will include construction of phase diagrams that help identify regions of the parameter space where high quality drops can be produced and efforts aimed at producing nanoscopic drops from microscopic nozzles. To tie the simulations and theory, the excellent agreement between computed predictions and scaling theories of pinch-off will be demonstrated. The excellent agreement between the simulation results and the experiments will be highlighted by means of photographs obtained with an imaging system that is capable of capturing 100 million frames per second. Since complex fluids cannot be characterized by their shear viscosity alone and drop formation involves predominantly extensional deformations, efforts underway to infer the extensional viscosity of such fluids will also be described.

11:20am **IJ+BI+MN-WeM11 The Microfluidics of NonSpherical Colloidal Particles and Vesicles with Application to Blood Additives**, ***E.S.G. Shaqfeh***, Stanford University **INVITED**

Many dispersions of colloidal particles with application in materials processing, biological assays, or medicine, contain elongated particles (e.g. ellipsoidal disks, rods, etc.) Recently these particles have been used in drug delivery applications because of the inability of leukocytes to easily rid them from the circulation. Moreover such particles are useful at the nanoscale for application in cancer therapies, either for detection of tumor vasculature or for the delivery of anti-cancer agents to tumor endothelial cells. Thus, the study of anisotropic particulate flows with adhesion in microchannels especially in mixtures with vesicle flows (i.e. red blood cells) has taken on a particularly important set of engineering applications. We will review our computer simulations of these processes with a view toward virtual prototyping and engineering these therapies.

Nanometer-scale Science and Technology
Room: L - Session NS-WeM

Nanoscale Devices and Sensors and Welch Award
Moderator: R.J. Colton, Naval Research Laboratory

8:00am **NS-WeM1 2009 Medard Welch Award Lecture - Molecular Interfaces to Nanoscale Materials: Making "Dumb" Materials "Smart"**, ***R.J. Hamers****, University of Wisconsin-Madison **INVITED**

Recent years have seen dramatic increases in the ability to synthesize new bulk and nanostructured materials. For many applications, such as sensing and renewable energy, the need for high stability drives a motivation for working with two classes of 'ultra-stable' materials: (1) nanoscale carbon, and (2) nanocrystalline metal oxides. While these materials are highly stable they do not provide important properties such as chemical or biological selectivity. Molecular surface chemistry can be used to turn these into "smart" materials by linking molecules that will convey chemical or biological selectivity for sensing or desirable electron-transport properties for applications in renewable energy. We have found that photochemical grafting of alkenes provides a nearly universal method for producing molecular monolayers on a wide range of highly stable materials. Surprisingly, this method works on both wide-bandgap semiconductors such as diamond and TiO_2, as well as metallic materials such as carbon nanofibers. Through a series of studies we have identified the underlying mechanism as an internal photoemission process in which ultraviolet light ejects an electron from the material into an adjacent reactive liquid, leaving behind a reactive (and persistent) hole that serves as a reactive site for molecular grafting. With suitable chemistry, this approach can be used to fabricate (bio)molecular interfaces with a high degree of functionality that can be used (for example) to achieve direct biological-to-electronic signal conversion for sensing. Recent work also shows this to be an excellent approach for novel types of electrocatalytic interfaces of interest for applications in renewable energy. In this talk I will discuss some of our efforts in making and understanding "smart" molecular and biomolecular interfaces to nanocrystalline materials, and some of the resulting applications in sensing and in renewable energy.

8:40am **NS-WeM3 Plasmon Induced Molecular Conductivity in Devices**, *P. Banerjee,* University of Maryland*, D. Conklin, S.U. Nanayakkara,* University of Pennsylvania*, T.-H. Park,* University of Michigan*, M.J. Therien,* Duke University*, **D.A. Bonnell***, University of Pennsylvania

Plasmonics and molecular electronics are two fields that explicitly exploit nanoscale physical phenomena. In the former, optical interactions with nanosized particles induce surface plasmons creating locally intense electric fields. In the latter, two decades of intense research has focused on electrical conduction in organic molecules to enable molecular electronics. The interaction of plasmons and electrical conduction has not been observed. Here we demonstrate the ability of a plasmon to alter the electrical properties of a molecular junction. Arrays of Au nanoparticles with different separations are assembled on an insulating substrate and functionalized with porphyrin compounds. These molecules posses unique optical properties and electron delocalization lengths on the order of 7-8nm. The wavelength and temperature dependence of transport in these hybrid devices reveal differences on photo conduction mechanism with wavelength. Three mechanisms are identified, one that operates in the dark current, one associated with electron-hole generation on absorption and one induced by surface plasmons. This ability of plasmons to directly influence electrical conductivity is a new mechanism of photoconduction that suggests a variety of optoelectronic applications.

9:00am **NS-WeM4 CMOS Compatible Silicon Nanowire Field Effect Transistor as Ultrasensitive Bio-sensor**, *S. Regonda, K. Trivedi, P. Fernandes, R. Tian, O. Seitz, J. Gao, E.M. Vogel, Y. Chabal,* ***W. Hu***, University of Texas at Dallas

Among the emerging devices for the future technology in the nanoscale regime, silicon nanowire (SiNW) devices have received significant attention for applications in logic gates, interconnects, photo detectors and biological and chemical sensors. For biosensing, femtomolar (fM) level detection of protein in solution has been demonstrated using both chemically synthesized nanowires [1] and lithographically defined nanowire field effect transistors (FETs) [2]. This type of sensor offers ultrasensitivity, rapid electronic readout, and does not require bulky sensing apparatus. It has a strong potential to be an ultra-portable and low cost biosensing platform that is badly needed for disease diagnostics and early detection.

In this work, we present our recent work on the similar nanowire FETs defined by e-beam lithography and standard Si processing technologies. This approach provides excellent manufacturability and feasibility of integrating circuitry with the sensor array on a single chip for ultimate system miniaturation and low manufacturing cost. In our process, SiNWs are defined by e-beam lithography in hydrogen silses quioxane resist, followed by a new two-step Si etch process, which is designed to improve the process reliability and controllability. SiNW FETs of 30-100 nm in widths, 10-30 nm in thickness, 5-80 µm in length have been successfully fabricated on Si on insulator (SOI) substrates. Uniform devices with sub threshold slope (SS) of 80 mV/dec and On/off ratio greater than 10^7 have been made reproducibly. We will present various device design and fabrication considerations for using nanoelectronic FETs as biosensors, e.g. source/drain doping effects, oxidation effects, plasma treatment effects, buffer solution effects and stability. These device issues are quite different from conventional use of nanowires in logic gates. We further integrate these SiNW FETs with SU8 microfluidic channels to detect proteins at low abundance in solution. Preliminary results have indicated a sensitivity or detection limit of 2fM. We expect to present controlled sensing results of protein biomarker under controlled flow conditions.

[1] Patolsky, F., Zheng, G and Lieber, C.M, *Nat.Protocols* 1, 1711-1724 (2006)

[2] Eric Stern, et al. *Nature* 445, 519-522 (2007)

9:20am **NS-WeM5 The Role of Surface Chemistry on the Properties of Nanoporous Gold**, ***J. Biener***, *M.M. Biener, A.V. Hamza,* Lawrence Livermore National Laboratory*, A. Wittstock, M. Bäumer,* Universität Bremen, Germany*, D. Kramer, R.N. Viswanath, J. Weissmüller*, Forschungszentrum Karlsruhe, Germany

Although surfaces or, more precisely, surface atoms determine the way how materials interact with their environment, the influence of surface chemistry on the bulk of the material is generally considered to be small. However, in the case of high surface area materials such as nanoporous gold the influence of surface properties can no longer be neglected. Therefore, actively controlling surface properties such as diffusion barriers and surface stress by surface chemistry should provide an opportunity to manipulate and fine-tune material properties. Specifically, we will show that surface chemistry is an important factor in determining the stability of

---

* Medard W. Welch Award Winner

nanostructured gold surfaces, and that macroscopic strain can be generated by surface-chemistry induced changes of the surface stress. The latter effect can be used to directly convert chemical energy into a mechanical response without generating heat or electricity first and thus opens the door to surface-chemistry driven actuator and sensor technologies.

Prepared by LLNL under Contract DE-AC52-07NA27344.

9:40am **NS-WeM6 Surface Plasmon Induced Enhancement of Hot Electron Flow Generated by Photons Probed with Metal-Semiconductor Nanodiodes**, ***J.Y. Park***, *H.S. Lee, J.R. Renzas, R. Baker, G.A. Somorjai*, University of California, Berkeley and Lawrence Berkeley National Laboratory

We present hot electron generation from photon absorption on metal-semiconductor Schottky diodes and its amplification by localized surface plasmon resonance. Hot electron flow was generated on a gold thin film (< 10 nm) by photon absorption and directly measured as a form of photocurrent on chemically modified gold thin film metal-semiconductor (TiO_2) Schottky diodes. The short-circuit photocurrent obtained with low energy photons (lower than the 3.1 eV bandgap of TiO_2) is consistent with Fowler's law, which confirms the presence of hot electron flow. The morphology of the metal thin film was modified to a connected gold island structure with a lateral length scale of 50- 100 nm after heating in oxygen. The nanometer scale domains in the gold island structures were electrically connected to the Ohmic pad, ensuring the measurement of the flow of hot electrons. These connected island structures exhibit a localized surface plasmon with peak energy at 550- 570 nm, which was separately characterized with UV-Vis. Hot electron flow (after normalizing photon absorption) was enhanced by a factor of three on the connected gold island structure. This result indicates correlation between the hot electron flow and localized surface plasmon resonance. Possible mechanisms for surface plasmon induced enhancement of hot electron generation are also discussed.

10:40am **NS-WeM9 Gallium Nanoparticles: An Alternative Metal for Surface-Enhanced Raman Scattering**, ***P.C. Wu***, *C.G. Khoury, T.H. Kim, Y. Yang,* Duke University, *M. Losurdo, G. Bruno,* IMIP-CNR, Italy, *T. Vo-Dinh,* Duke University, *H.O. Everitt,* Army AMRDEC, *A.S. Brown*, Duke University

The recent increased use of surface-enhanced Raman spectroscopy (SERS) for chemical and biological sensing is intimately tied to the surging interest in developing plasmonic metallic nanostructures. Typically silver or gold, SERS substrates exploit the plasmon resonance and the associated localized surface fields to enhance Raman scattering from the molecule of interest. We will present an alternative plasmonic metal, gallium, for use as SERS substrates. Gallium's prevalence in optoelectronic device growth also suggests their potential for integrated SERS structures. Our previous work has demonstrated interesting properties of gallium that make it an attractive metal for SERS sensing schemes compared to Ag or Au; these include its thermal and oxidative stability. Also in contrast to the properties of Ag and Au, Ga plasmonic nanoparticles can be tuned for size resulting in a plasmon resonance that varies from the near IR through the visible and into the deep UV.

Gallium nanoparticles (NPs) deposited onto dielectric substrates (glass and sapphire) were grown by molecular beam epitaxy. Nanoparticles were tuned to different plasmon resonances (i.e. mean size) to discern the effect NP geometry (size, distribution, and interparticle spacing) has on the strength of the Raman enhancement. In this work, solutions of the standard Raman dye Cresyl Fast Violet were dropcast onto the NP substrate at varying concentrations to evaluate the linear correlation between SERS intensity and molecular concentration. Direct comparison between bare (unmetallized) surfaces and metallized surfaces were made to quantify the Raman enhancement resulting specifically from the presence of Ga NPs. The enhanced Raman signal in the presence of Ga NPs suggest that Ga NP are effective alternatives to Ag and Au for SERS applications.

11:00am **NS-WeM10 Effect of Functional Substrates on Optoelectronic Properties of Hybrid Nanostructures**, ***D. Conklin***, University of Pennsylvania, *P. Banerjee,* University of Maryland, *S.U. Nanayakkara,* University of Pennsylvania, *T.-H. Park,* University of Michigan, *M.J. Therien,* Duke University, *D.A. Bonnell*, University of Pennsylvania

Functionalized gold nanoparticles are assembled on ferroelectric and non ferroelectric substrates. The assemblies are designed to exhibit photoconductivity by controlling particle size, distribution, density, and by linking with optically active porphyrin complexes. The wavelength and temperature dependence of transport is used to determine the effect of the substrate on the optoelectronic properties. Specifically, the effect of substrate local field due to the domain polarization is determined by comparing the response of similar nanostructures on non ferroelectric (SiOx) substrates. Activation energies of high temperature transport mechanisms and tunneling parameters of low temperature transport mechanisms are compared. The combination of optoelectronic molecular nanostructures and a functional substrate suggests new device strategies.

11:20am **NS-WeM11 Control of Coupled Silicon Atomic Quantum Dots for Nano-Electronic Computing Architectures**, ***J. Pitters***, National Institute for Nanotechnology, Canada, *B. Haider,* University of Alberta, Canada, *G. Dilabio,* National Institute for Nanotechnology, Canada, *L. Livadaru, J. Mutus, R. Wolkow*, University of Alberta, Canada

Coupled quantum dots form an attractive basis both for fundamental studies of single electron control and as potential building blocks for future nano-electronic devices. One computing scheme, Quantum-dot Cellular Automata (QCA), is based upon "cells" of tunnel coupled quantum dots and electrostatic interactions between adjacent cells to transmit binary information and perform calculations with minuscule power consumption. Efforts to fabricate electrostatic QCA devices have been limited by the need for extreme cryogenic conditions. We have demonstrated a new approach using the scanning tunneling microscope (STM) at room temperature. We show that the silicon atom dangling bond (DB) state, on an otherwise hydrogen terminated surface, serves as a quantum dot. These atomic quantum dots can be assembled into multi-DB ensembles through precise hydrogen atom removal using the STM tip. Assembly at critical distances leads to electron tunnel coupling between DBs and control over the net electron occupation of assembled quantum dot DBs is also demonstrated. Additionally, it is shown that a pair of tunnel-coupled DBs can be switched, using electrostatic control, from a symmetric bi-stable state to one exhibiting an asymmetric electron occupation. Similarly, the setting of an antipodal state in a square assembly of four DBs is achieved, demonstrating at room temperature the essential building block of a quantum cellular automata device.

11:40am **NS-WeM12 Towards Wafer-Scale Fabrication of Room-Temperature Single-Electron Transistors**, *P. Bhadrachalam, V. Ray, R. Subramanian,* ***S.J. Koh***, University of Texas at Arlington

We recently demonstrated CMOS-compatible fabrication of single-electron transistors (SETs) that operate at room temperature (Nature Nanotech. V.3, p.603, 2008). This was realized using a new device architecture in which source and drain electrodes are vertically separated with a Coulomb island placed between the electrodes. Here, we present two important advancements toward wafer-scale fabrication of room-temperature SETs for practical applications. Firstly, we present a technique for placing Coulomb islands between the source and the drain electrodes with nanoscale precision, which significantly improves the yield of device fabrication. This accurate placement was made possible by electrostatically guiding Coulomb islands onto the center of the electrode gap. The electrostatic guiding structures were made on a large scale using self-assembled monolayers (SAMs) of positively- and negatively- charged molecules. Secondly, we present a very small fluctuation of the background charges for our fabricated SETs. The uncontrolled fluctuation of background charges has been one of the major obstacles to the practical implementation of SET devices. The shift of background charges was directly measured from the phase shift of Coulomb oscillations at room temperature and it was found that the charge shift was only ~0.01*e* (*e*: electron charge) over a time span of more than a week. These two advancements show a great promise for realization of integrated systems of room-temperature SETs for practical use. (Supported by NSF CAREER (ECS-0449958), ONR (N00014-05-1-0030), THECB (003656-0014-2006))

Plasma Science and Technology
Room: A1 - Session PS1-WeM

Plasma Diagnostics, Sensors, and Control I
Moderator: G. Upadhyaya, Lam Research

8:00am **PS1-WeM1 A New Diagnostic Tool of Electron Energy Distribution Function in Capacitive Mode Plasmas in a Variety of Frequencies**, *H. Shindo,* ***Y. Nakazaki***, Tokai University, Japan

A new diagnostic tool to measure Electron Energy Distribution Function (EEDF) by an emissive probe has been proposed[1] and applied to radio-frequency (RF) plasmas. In particular, the measurements are made, focused on the condition in which the mode transition from the capacitive to the inductive is occurred at the frequencies of 2 to 60 MHz. It is generally difficult for a conventional probe method to measure EEDF in RF plasmas, because of the plasma potential fluctuation, particularly in the capacitive mode. On the contrary, one of the advantages of the present method is that the measurements are free from the high frequency potential fluctuation.

The method is based on measurement of the functional relationship between the floating potential change ΔV_F and the heating voltage V_H of emissive probe. If the Maxwellian plasma is concerned, a practical and useful equation for ΔV_F can be obtained as in [1]. It is important to know that the value of ΔV_F contains information of electron energy distribution with several electron volt interval along the floating potential V_F, because ΔV_F is determined only by the current of plasma electrons with an energy interval.

In the experiments, the values of ΔV_F were measured in the Ar plasmas which were produced by a single-loop antenna[2] in the frequencies of 2 to 60 MHz and the gas pressures of 5 to 100 mTorr. The values of ΔV_F behave quite differently, depending on the frequency and the gas pressure, hence the plasma mode. It is found that in the inductive mode appeared at the pressures above 20 mTorr at 2 MHz, 30 mTorr at 13 MHz, the value of ΔV_F is consistent with the above-cited equation, enabling to determine the electron temperature, while in the capacitive mode appeared below abovementioned pressures and at 60 MHz, the behavior of floating potential change ΔV_F is fairly complicated, hence non-Maxwellian plasma. In all capacitive modes, from the data set of ΔV_F and V_F, the electron energy probability function (EEPF) is calculated, and the EEPF thus obtained reveals a bi-Maxwellian with the two electron temperatures depending on the frequencies. It should be emphasized that the present diagnostic method becomes powerful in observation of the plasma mode transition in a variety of frequencies.

References:

[1] K.Kusaba and H.Shindo, Review of Scientific Instruments, **78**, 123503-1(2007).

[2] Y.Jinbo and H.Shindo, Applied Physics Express, **2**, 016001-1(2009).

8:20am **PS1-WeM2 A Diagnostic Investigation of Pulsed PECVD for Thin Film Deposition**, ***C. Lange***, *C.A. Wolden*, Colorado School of Mines

Low frequency (~1 Hz) pulsed PECVD is an alternative approach for self-limiting growth of high quality thin films at high rate and with good conformality. This technique raises a number of new questions with respect plasma ignition and dynamics. Critical questions include the role of metal precursors in the gas phase as well as those that adsorb to chamber surfaces when the plasma is off. To gain a more fundamental understanding of this process we have built a reactor with a diagnostics suite that includes I-V measurements, Langmuir probe, optical emission spectroscopy (OES), quadrupole mass spectrometry (QMS). In this paper we will present transient measurements from these techniques that are acquired in registry with the plasma pulse waveform. Relevant time scales in this system range from microseconds for application of a stable voltage waveform to seconds for mass transfer and chemical reactions. These critical time scales in the process are experimentally determined. Results will be compared to detail computational models. To decouple the complexities of this process comparisons are made among systems of increasing complexity. These include a baseline O_2/Ar plasma, continuous wave PECVD, plasma-enhanced ALD, and finally pulsed PECVD.

8:40am **PS1-WeM3 Characterization and Active Stabilization of Plasma and Generator Interactions**, *V.L. Brouk*, ***D. Carter***, Advanced Energy Industries, Inc., *J. Roberg*, Advanced Energy Industries, Inc

Plasma instabilities are often seen in low power, low pressure, electronegative discharges. Instabilities affecting particle density, optical emission and coil voltage have been observed with oscillation frequencies ranging from a few hundred hertz to well over one hundred kilohertz [1,2]. While instabilities can be inherent to plasma conditions it is well known that power delivery plays an important role in promoting or propagating the behavior. A study of the mutual interaction between RF amplifier and plasma impedance shows the alignment between impedance trajectory and the power profile contours of the generator is critical in determining a system's sensitivity to instabilities. Reactive elements in the delivery path can be used to rotate impedance trajectories but the recent advent of variable frequency RF supplies has provided a more convenient means for trajectory rotation and active stabilization. In this work we empirically evaluate these behaviors and demonstrate the utility of RF frequency as a controllable parameter for plasma stabilization. In defining an active stability control system, we demonstrate measurements for detecting and quantifying instabilities. Instability oscillation frequency offers insight into the nature of parasitic feedback from mutual generator-plasma interaction and thus we show how discriminating instability frequency is also useful in defining an intelligent stability control system.

1) A. M. Marakhtanov, et. al., J. Vac. Sci. Technol. A 21 (6), Nov/Dec 2003

2) A. Descoeudres, et. al., Plasma Sources Sci. Technol. 12 (2003) 152–157

9:00am **PS1-WeM4 Plasma Characterization of a 200-mm Hollow Cathode Magnetron for the Deposition of Metallic and Compound Thin Films**, ***L. Meng***, *R.E. Flauta, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

The hollow cathode magnetron (HCM) is a high density plasma tool developed for ionized physical vapor deposition (I-PVD) used for high-aspect ratio thin film interconnects. To better understand the fundamental mechanisms of the HCM device performance and consequently obtain the control to ensure highly conformal and uniform thin film deposition, it is necessary to study the plasma conditions and correlate them to the resultant thin film properties. A commercial high power 200-mm INOVA HCM deposition tool from Novellus was characterized using a 3-D scanning Langmuir probe that was specifically engineered for the intense metal plasma present. This yielded a spatial resolution of both electron density (n_e) and temperature (T_e). In addition, a gridded energy analyzer (GEA) was integrated with quartz crystal microbalance (QCM) to determine the ionization fraction of the metal flux reaching the substrate. With an increasing input power in the range of 0-16 kW, T_e at the substrate decreased from 3 to 1 eV while n_e increased from 6×10^{10} to 2×10^{12} cm^{-3}. A decreasing pressure also increased the electron density. The 3-D spatial distribution of n_e and T_e in the HCM tool revealed a higher n_e and lower T_e at the center of the plasma than at the edge. These results strongly correlated to the resultant film deposition quality and uniformity on the substrate. The deposition rate of metal flux was recorded with QCM, while the GEA was adjusted to repel or admit the metal ions to allow for an ionization fraction of the metal atoms to be calculated. This fraction varied from less than 10% to over 90% depending on the input power and pressure conditions. Lower HCM power increased the ionization fraction due to the corresponding higher T_e and thus higher ionization cross section. At higher pressures, the ionization was enhanced because of the greater residence time of atoms in the plasma. The ion energy distribution was also studied using the GEA/QCM tool. These plasma diagnostics measured the resultant mechanisms of the HCM and provided a matrix of parameters such as T_e, n_e, metal ionization fraction, ion energy and deposition rate to allow for optimization of the deposition process. Ta and TaN thin films were then formed on Si substrates using Ar or Ar/N_2 sputtering plasmas, respectively. These films were characterized through the use of scanning electron microscopy (SEM), X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS) to determine the microstructure, crystal quality, and stoichiometry of the deposited film. The film properties were found to be affected by the HCM power, pressure and the sample locations, and correlated with the plasma parameters.

9:20am **PS1-WeM5 Probe Measurements in a Very High Frequency CCP Discharge**, ***L. Dorf***, *S. Rauf, K. Ramaswamy, K. Collins*, Applied Materials **INVITED**

Langmuir probe (LP) measurements in a realistic very high frequency (VHF) capacitively coupled plasma (CCP) discharge are complicated by a number of factors, such as absence of a well-defined DC ground reference and unpredictable behavior of standard electronic components at VHF. The amplitude of RF potential in a VHF CCP discharge can be large (few tens of volts), especially compared to that in an ICP discharge with similar parameters. RF potential distorts both electron and ion parts of the measured probe V-I characteristic, resulting in unrealistic plasma parameters, and therefore needs to be compensated for. Here, we present results of measurements performed in a 300 mm 162 MHz dielectric plasma etcher using a compensated LP (CLP) and a floating double probe (DP). Probe designs employ a number of previously developed techniques. The probes were used to study the effects of magnetic field, input power, pressure, and chemistry on plasma density radial profiles. The electron part of the CLP V-I characteristic was also used to study the effect of the input power on the electron energy distribution function (EEDF). For all operating conditions – input power of 100 - 1400 W and neutral pressure of 10 - 300 mT – the measured electron temperature was found to lie in the range of 2 - 4 eV, and the plasma density in the range of a few 10^{10} to a few 10^{11} cm^{-3}, increasing with power. In Argon, at 10 – 50 mT, the density was found to increase with pressure (due to higher ionization rate). At higher pressure, 50 – 100 mT, the density profile was found to become more uniform, but no significant change in maximum density was observed; further increase in pressure (100 - 300 mT) leads to a decrease in plasma density. Applying a magnetic field of a few tens of Gauss (generated by solenoidal coils placed above the top electrode) was confirmed to have a significant effect on the radial density distribution. Due to a difference in electron residence time caused by the difference in field lines geometry, edge density increases with magnetic field, whereas center density decreases. In electronegative chemistries, the effects of pressure and magnetic field are different. Namely, in O_2 at 15 – 100 mT: (a) positive molecular ion density decreases with pressure (possibly due to higher attachment), and (b) center density decreases with magnetic field, but edge density remains largely unchanged. In CF_4, the effect of pressure is similar to that in O_2, whereas the effect of magnetic field is like that in Ar at low pressure (15 mT), and like that in O_2 at high pressure (100 mT). Experimental results were found to be in general agreement with results of applicable simulations.

10:40am **PS1-WeM9 Macroscopic Diagnostics for In-Situ Measurement of Sidewall Charging During Plasma Etching**, ***E. Ritz***, *J.A. Hoban, M.J. Neumann, D.N. Ruzic*, University of Illinois at Urbana-Champaign

In plasma etching processes, especially those with high aspect ratios, the leading type of manufacturing defects that occur are trenching, bowing and twisting. These defects cause failures in semiconductor devices such as processors and DRAM. In order to investigate the role of feature sidewall charging on these defects, a series of macroscopic diagnostics were implemented which are capable of measuring time-resolved charge buildup at several points along a feature profile. This in-situ diagnostic consists of alternating conducting and insulating layers made of copper and teflon, respectively, with an axial hole that acts as the feature via. The insulating layers create discrete measurement layers, provided by the copper electrodes, which can be independently monitored inside of a commercial etching tool in real time to determine how the incident current from the plasma varies along the feature depth. By measuring the current reaching the bottom of the feature, as compared to the mid-plane or the top, one can determine the influence of sidewall charging. To determine the effect of geometry on charging, several aspect ratios were used by maintaining the same device height but varying the diameter of the via. The entire diagnostic is 19.2mm tall with aspect ratios from 5:1 to 10:1. Plasma and charging experiments were conducted in a commercial silicon dioxide etch chamber with three available frequencies (2.0 MHz, 2.2 MHz, and 13.56 MHz) thus allowing study of frequency-dependent charging, as well. Typical powers ranged from 300W to 1000W resulting in sidewall current measurements on the order of milliamps. Typical plasma densities are $2*10^{12} \pm 5*10^{11}$ cm^{-3} and electron temperatures are 3 ± 0.3 eV. Results from the diagnostics are shown for various plasma conditions and compositions.

11:00am **PS1-WeM10 Study on Relation between CFx Radicals and Plasma Parameters in ICP Plasmas with Laser-Induced Fluorescence and Wave Cutoff Probe**, ***J.-H. Kim***, Korea Research Institute of Standards and Science (KRISS), *K. Rho*, KAIST, South Korea, *Y.-S. Yoo, S.-J. You, D.-J. Seong, Y.-H. Shin*, KRISS, South Korea

The behaviors of CF and CF2 radicals were studied in CF4 inductively coupled plasma. CF and CF2 radicals were measured using a laser-induced fluorescence method [1,2]. Absolute electron density was measured using a cutoff probe [3], and the electron temperature was measured using a Langmuir probe to study relation between the electron property and radicals. CF and CF2 densities are drastically changed by variations of operating pressure, ratio of mixed gases and RF source power. To examine the relation between electron density and CF and CF2 radicals, CF, CF2 radical and electron density were measured as varying the RF power which is a major external parameter influencing to the electron density. As the RF power was increased, CF and CF2 radical density increased in the range of low electron density and then decreased over a critical electron density. Dependence of CF and CF2 radical density on the electron density was theoretically analyzed with rate equations. The theoretically analyzed relation between the electron density and the radical density was in good agreement with the experimental result.

[1] G. Cunge, P. Chabert and J.P. Booth, J. Appl. Phys. V89, p7750 (2001)

[2] S. Hayashi, K. Kawashima, M. Ozawa, H. Tsuboi, T. Tatsumi, and M. Sekime, Sci. and Tech. Adv. Mat. V2, p555 (2001)

[3] J.H.Kim, D.J.Seong, J.Y.Lim, and K.H.Chung, Appl. Phys. Lett. V83, p4725 (2003)

[4] J.H.Kim, K.H. Chung and Y-S Yoo, J. Korean Phys. Society. V47, p249 (2005)

11:20am **PS1-WeM11 Development of High Density Radical Source and the Behaviors of Radicals in N_2-H_2 Mixture Plasma**, ***S. Chen***, Nagoya University, Japan

Dry processes using nitrogen atoms are essential to nitride semiconductor device fabrications such as nitridation, etching damage restoration or nitrogen doping technologies. To reduce the processing time and improve the film quality, the high density radical source with high efficiency and stability is strongly required. So far, some kinds of radical sources have been evaluated and characterized qualitatively using optical emission spectroscopy (OES). However, the absolute density could not be measured by the OES. In this study, we have developed a new high density radical source (HDRS) and measured the absolute density of atomic radicals by using vuacuum ultraviolet absorption spectroscopy (VUVAS).

The HDRS was designed by optimize the number of antenna coil turns in ICP. The ICP with 4 turns coil antenna enabled us to obtain the highest N atomic radical density. It was found that the radical density was significantly dependent on the power density, plasma density and gas temperature. N radical density was increasing from $7.3x10^{11}$ to $3.6x10^{12}cm^{-3}$ with pressure increases from 0.025 to 0.5Pa. These results show the N radical density was one order magnitude higher than traditional source. In the power dependence of radical density, the radical density was increased with increase the powers up to 400W and saturated.

The HDRS was also characterized using N_2-H_2 gas mixture. Relative changes of N, H and NH_3 densities were measured as a function of the N_2 flow rate ratio. NH_3 was measured by Quadrupole Mass Spectroscopy (QMS). In this experiment, the total pressure N_2/H_2 was fixed at 0.5Pa. When N_2/H_2 ratio increased from 10% to 33.3%, the absolute density of H radical was increased from $2.3x10^{12}$ to $4.1x10^{12}cm^{-3}$. Absolute density of N radical increased from $2.3x10^{11}$ to $1.7\ x10^{12}cm^{-3}$. At the N_2/H_2 ratios beyond 33.3%, the N radical density increased to $2.1x10^{12}cm^{-3}$, but H density decreased to $3.2x10^{11}cm^{-3}$. In this experiment, the behaviors of NH_3 relative density agreed with those of H radical. When the N_2 flow rate ratio of 33% was fixed and the pressure was varied from 0.025 to 0.35Pa, it was found that the H radical density was higher than N radical density, but at pressures of above 0.35Pa the N radical density increased rapidly to $5.1x10^{11}cm^{-3}$ and H radical density increased to $3.4x10^{11}cm^{-3}$. As a result, the behaviors of radicals in N_2-H_2 mixture plasma were investigated and the mechanism of radical kinetics in HDRS was discussed.

Plasma Science and Technology
Room: B2 - Session PS2+TF-WeM

Plasma Deposition and Plasma-assisted ALD
Moderator: E.R. Fisher, Colorado State University

8:00am **PS2+TF-WeM1 Plasma Polymerization of bis-1, 2-(triethoxysilyl) Ethane (BTSE): Interfacial Characterization by ToF-SIMS and XPS**, ***A. Batan***, Univ. Libre de Bruxelles, Facultés Univ. Notre-Dame de la Paix, Belgium, *N. Mine, B. Douhard,* Facultés Univ. Notre-Dame de la Paix, Belgium, *F. Brusciotti, I. De Graeve, J. Vereecken,* Vrije Univ. Brussel, Belgium, *M. Wenkin, M. Piens,* Coating Research Inst., Belgium, *H. Terryn,* Vrije Univ. Brussel, Belgium, *J.J. Pireaux,* Facultés Univ. Notre-Dame de la Paix, Belgium, *F. Reniers*, Univ. Libre de Bruxelles, Belgium

Plasma polymerized BTSE films were deposited by vacuum and atmospheric plasma on aluminum (99.99%) substrate. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used for probing the metal/film interface. Ion etching by Xe+ 500 eV and 250 eV, depending on the plasma polymer BTSE film thickness, exposed the interfacial region, while Ga+ (15 keV) ions analysed the material composition.

An AlOSi+fragment was identified at nominal mass m/z = 70.9539 amu in high mass resolution spectra. The presence of this aluminium-oxygen-silicon ion fragment is a strong indication of an existing chemical interaction between the plasma polymer BTSE film and the aluminum substrate: the nature of this interaction implies the formation of a covalent bond between the silane and the aluminum substrate. Until now, this strong interaction silane-aluminum has never been observed in plasma polymer BTSE films.

Ageing tests combined with X-ray photoelectron spectroscopy measurements allowed the evaluation of the adhesion performance of plasma polymerized BTSE films on aluminum. The Si2p signal intensity was measured before and after dipping the coated sample in an ultrasonic water bath for 30 min, at room temperature. The Si2p peak intensity remained constant after the sonication test, showing a strong adhesion between the deposited layer and the aluminum substrate.

Acknowledgements

The project partners VUB, ULB, FUNDP and CoRI gratefully acknowledge the Belgian Science Policy for funding the FOMOS project (P2/00/04) in the "Programme to stimulate knowledge transfer in areas of strategic importance". www.belspo.be

8:20am **PS2+TF-WeM2 Self-limiting Deposition of Nanolaminates by Pulsed PECVD**, *P.C. Rowlette*, ***C.A. Wolden***, Colorado School of Mines

Self-limiting synthesis of alumina-titania nanolaminates (ATO, Al_2O_3/TiO_2) was accomplished via pulsed plasma-enhanced chemical vapor deposition. At the synthesis temperature of 150 °C the alumina layers were amorphous, while TiO_2 layers displayed a polycrystalline anatase structure. Digital control over nanolaminate structure was demonstrated through elemental analysis and TEM imaging. The optoelectronic properties of the ATO structures were examined as a function of composition and bilayer thickness. C-V measurements showed that the effective dielectric constant (κ) of the nanolaminates was consistent with treating the structure as individual capacitors in series. I-V measurements showed that leakage current deteriorated with TiO_2 content, though low leakage was restored through interfacial engineering. With respect to dielectrics these results suggest that the best nanolaminate would employ Al_2O_3 interface layers deposited by PE-ALD to minimize leakage current, and that these two layers would sandwich a single TiO_2 layers whose thickness would set the effective dielectric constant. We will also present work in SiO_2 –TiO_2 nanolaminates formed by the same technique at room temperature with applications as optical components. Finally, we will present recent findings in the area of inorganic/organic hybrid nanolaminates formed by alternating oxide and polymer layers.

8:40am **PS2+TF-WeM3 Tailoring PECVD Ultra-Low-k Films for Nanoscale Interconnects**, ***E.T. Ryan***, GLOBALFOUNDRIES, *S.M. Gates, S. Cohen, Y. Ostrovski, V. Patel, E. Simonyi, C. Dimitrakopoulos,* IBM T.J. Watson Research Center*, A. Madan,* IBM Microelectronics*, G. Dubois,* IBM Almaden Research Center*, A. Grill*, IBM T.J. Watson Research Center **INVITED**

Ultra-low-k (ULK) insulating films are critical to reduce the resistance-capacitance (RC) delay in interconnect wires. This talk will briefly review the history of low-k materials that culminated with ULK nanoporous organosilicate glass (also called pSiCOH) films deposited by plasma-enhanced chemical vapor deposition (PECVD).

Nanoporous ULK pSiCOH films pose many interconnect fabrication challenges, and the needs of integration impose limits on the material properties of the films. For example, the pSiCOH film can be damaged by exposure to other plasma processes, and the degree of damage is related to material properties such as porosity, pore size, pore interconnection, carbon content, and bonding arrangement.

The stress and mechanical strength (modulus) of the pSiCOH film is critical for the structural stability of the interconnect wires. Spontaneous cracking is directly related to both modulus and stress. Packaging imposes additional stresses on the interconnect lines. Furthermore, if the modulus of the ULK film becomes too low, capillary forces during post-etch wet cleaning can cause the patterns in the pSiCOH film to collapse.

These integration needs require balancing various trade offs in material properties, and this constrains the process space for pSiCOH film deposition. The talk will review our work to design pSiCOH films with different properties to meet different integration needs. Examples of PECVD films with properties tailored to meet these interconnect needs illustrate the trade offs we face.

First we review our efforts to design films that are resistant to damage by the plasmas used for etch and ash and cap deposition. Mechanical properties were also maintained at favorable values. We modified a conventional pSiCOH film (V1) prepared from DEMS and BCHD porogen by adding a carbosilane skeleton precursor to incorporate new carbon structures. The modified films (V2, V3) can be adjusted by the choice of the carbosilane precursor. The films were characterized for electrical and mechanical properties, pore characteristics, and FTIR. The plasma damage of the films was characterized by thickness loss after HF etch of the damaged layer and depth profiling by ToF-SIMS. The new pSiCOH V2 and V3 films show reduced plasma damage. Our effort to optimize the pSiCOH modulus will be discussed, with the overall goals of reducing plasma induced damage and maintaining favorable stress and modulus.

9:20am **PS2+TF-WeM5 Amplitude Modulated Pulse RF Discharges for Producing and Driving Nano-Blocks**, ***S. Iwashita****, *H. Miyata, H. Matsuzaki, K. Koga, M. Shiratani*, Kyushu University, Japan

We have proposed a bottom-up nanosystem-fabrication method, which consists of production of nano-blocks and radicals (adhesives) in reactive plasmas, transport of nano-blocks towards a substrate, their arrangement on the substrate using pulse RF discharges with the amplitude modulation (AM) of the discharge voltage. For the method, control of the size of nano-blocks and their manipulation without their agglomeration are important. Up to now, we have succeeded in controlling the size of nano-blocks by pulse RF discharges,[1] and have realized their rapid transport from their generation region towards a substrate with suppressing agglomeration by pulse RF discharges combined with AM.[2,3] Here we report a criterion for driving nano-blocks rapidly and discuss their transport mechanisms.

Experiments were carried out using a capacitively coupled RF discharge reactor described elsewhere.[1-3] Nano-blocks were formed in 13.56 MHz RF discharges of $Si(CH_3)_2(OCH_3)_2$ diluted with Ar. Nano-block transport in AM discharges is classified into two kinds: one is the rapid transport at a velocity more than 60 cm/s during the modulation period and the other is the slow transport at a velocity of 3-5 cm/s after turning off discharges due to temperature gradient. The key parameters to the rapid transport are the period Δt and voltage V_{AM} of the modulation and asymmetry of the discharges, which is characterized by the dc self-bias voltage V_{dc}. The larger nano-blocks need longer Δt, higher V_{AM}, and higher V_{dc}, for their rapid transport because of their large inertia. All nano-blocks of 26 nm in size, for instance, are transported rapidly during the modulation period for V_{dc} = -412 V, Δt = 100 ms and V_{AM} = 1076 V, while 54 % of them transported rapidly during the modulation period and 46 % of them are transported after turning off discharges for V_{dc} = -350 V, Δt = 100 ms and V_{AM} = 883 V. Just after the initiation of the modulation, electrostatic force drives nano-blocks, and then ion drag force drives them towards a substrate. It should be noted that although most nano-blocks are neutral, some of them turn into ones charged negatively due to charge fluctuation and such nano-blocks charged negatively are driven by electrostatic and ion drag forces. The method was applied to deposition of nano-block composite porous low-k films and dielectric films of k = 1.4 and Young's modulus above 10 GPa were realized.

[1] S. Nunomura, M. Kita, K. Koga, M. Shiratani, and Y. Watanabe, J. Appl. Phys., **99**, 083302 (2006).

[2] K. Koga, S. Iwashita, and M. Shiratani, J. Phys. D: Appl. Phys., **40**, 2267 (2007).

[3] M. Shiratani, K. Koga, S. Iwashita, and S. Nunomura, Faraday Discuss., **137**, 127 (2008).

9:40am **PS2+TF-WeM6 Plasma Deposition of Platinum-Based Nanocomposite Films as Fuel Cell Electrocatalysts**, ***A. Milella***, *E. Dilonardo,* University of Bari, Italy*, F. Palumbo,* Institute for Inorganic Methodologies and Plasmas (IMIP)- CNR, Italy*, S. Martin,* CEA-G/ Leti, France*, R. d'Agostino, F. Fracassi*, University of Bari, Italy

In Proton Exchange Membrane Fuel Cells (PEMFC) the electrode reactions rely heavily on the use of platinum catalysts. Since cost of this precious metal is one of the main barriers for commercialization of fuel cells, many research efforts are addressed to obtaining higher catalytic activity than the standard carbon-supported platinum particle catalysts used in current PEM fuel cells, with a reduced amount of metal. In this framework, plasma processes are particularly appealing since they allow the dispersion of catalyst in form of nanoparticles and the control of the film thickness to the nanometer scale. Few examples are present in literature concerning the use of low pressure plasma for platinum-containing films as catalytic electrodes.

In this contribution we report our latest results on the one-step deposition of nanocomposite thin films containing platinum nanoclusters (high specific area), with definite concentration and uniform in size. Thin films are obtained from a simultaneous plasma-enhanced chemical vapour deposition of ethylene (C_2H_4) / argon gas mixtures and RF sputtering of a platinum target. The main advantages of this approach consist in the reduced thickness (less then 1 micron), the possibility to coat complex shapes, and the easy scale up in a continuous process. A comprehensive study on the effect of different parameters (RF power, deposition time, gas flow rates) on the film chemical composition and structure will be presented. In particular, it will be shown that the platinum content in the film, determined by X-ray Photoelectron Spectroscopy (XPS), can be continuously varied by properly controlling the RF power and the monomer flow rate. Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) shows that films are porous with a cross-section characterized by columnar structures of different size and orientation, depending on the deposition parameters. Transmission Electron Microscopy (TEM) confirms that platinum aggregates in crystalline nanoclusters of diameters in the range 3-7 nm, uniformly distributed in the film. The electrochemical active area of the films, as determined from *ex-situ* Cyclic Voltammetry (CV) analyses, reaches a maximum correspondingly to a platinum load of about 60%. Preliminary results on device testing will be also presented.

Acknowledgments

This work was founded by the European Project *NAPOLYDE* (NMP2-CT-2005-515846).

10:40am **PS2+TF-WeM9 Contribution of CN Radicals to the Nitrogen Content of Plasma-Deposited a-CN_x Materials**, ***J.M. Stillahn****, *E.R. Fisher*, Colorado State University

This work details our efforts to explore the plasma-enhanced chemical vapor deposition of amorphous carbon nitride (a-CN_x) materials, which exhibit a variety of interesting physical and chemical properties. These properties depend critically on the manner and extent to which nitrogen is substituted into the amorphous film network, but the mechanisms responsible for nitrogen incorporation are often obscured by the

---

* PSTD Coburn-Winters Student Award Finalist

complexities of mixed-precursor systems (e.g., CH_4/NH_3) that are frequently used to study a-CN_x deposition. Single-source precursors (e.g., CH_3CN, BrCN) help to simplify the gas phase chemistry, and in this work we have employed such precursors to learn about nitrogen incorporation mechanisms in more complex systems. The CN radical is examined with particular interest as it exhibits near-unity surface reaction probabilities under all conditions, providing a stark contrast with other N-containing plasma species such as the less-reactive NH radical. Interestingly, this difference in surface reactivity is echoed by disparities in the molecules' internal energies, which are characterized in this work by the rotational temperature. The contributions of the CN radical become especially evident with the use of BrCN plasmas, yielding films that delaminate and buckle upon exposure to atmosphere. This behavior may reflect a high concentration of terminating groups in the film, leading to a porous material that is compressively stressed as it absorbs water. Data such as these can be used to form a more complete understanding of the chemical mechanisms that lead to a-CN_x deposition.

11:00am **PS2+TF-WeM10 Comparison between a DC Reactive Magnetron Sputtering Discharge in an Ar/NH_3 and $Ar/H_2/N_2$ Gas Mixture**, ***F. Henry***, *A. Batan, F. Reniers*, Université Libre de Bruxelles, Belgium

The reactive magnetron sputtering technique is widely used for thin films deposition. This one offers many advantages like: a large choice of composition of the deposited films, a low temperature of deposition that allows to use a large scale of substrates and a high speed of deposition. Other techniques used for thin films deposition like CVD often required the use of hazardous gases and required a high temperature of deposition.

In this study, two different gas mixtures (Ar/NH_3 and $Ar/H_2/N_2$) used for the deposition of silicon nitride thin films were compared. Optical Emission spectroscopy spectrum (OES) were recorded to characterize the plasma gas phase. X-ray Photon-electron Spectroscopy (XPS) was used to determine the stoichiometry of the deposited thin films and used to perform a depth profiling of the silicon target after exposure to the reactive magnetron sputtering discharge. Optical interferometry was used to measure the film thickness and current-voltage curves were plotted to determine the electric characteristics of the discharge.

The influence of the plasma parameters such as the molar fraction of reactive gas and the total pressure was studied. The same parameters were investigated for both kind of gas mixture and a detailed comparison was performed.

The experiments were performed in a stainless steel chamber equipped with a home-made magnetron cathode. The total pressure was set between 5×10^{-3} Torr and 2×10^{-2} Torr and the molar fraction varied between 0 and 0.6 in reactive gas. During all experiments the discharge current was set to 300 mA.

The excited species detected into the Ar/NH_3 and $Ar/H_2/N_2$ plasma were the same, except for the NH radical that was not detected in the $Ar/H_2/N_2$ plasma.

The stoichiometry of the thin films deposited with the two kind of gas mixtures was investigated by XPS, a N/Si ratio of 1.33 was determined for the $Ar/H_2/N_2$ plasma and 1.22 for the Ar/NH_3 plasma.

The current voltage curves were plotted at different molar fractions of reactive gas and at different total pressures. A typical drop of the tension due to a poisoning of the target was observed for the Ar/NH_3 plasma and for the $Ar/H_2/N_2$.

11:20am **PS2+TF-WeM11 The Application of AC Diode Sputtering for Aluminum Thin Films in Small Apertures**, ***D.R. Walters***, Argonne National Laboratory

A thin conductive film was applied on the inner surface of a small-aperture vessel using the AC Diode Sputtering process. This paper describes the process and the technical equipment used in this thin-film method. The process configuration presented here employs a dual-electrode arrangement, which creates a glow discharge field around both electrodes, thereby spreading out the affected area. An example of coating performed in a 5 mm by 12.5 mm rectangular channel by 3.4 m in length is present along with examples of circular cross-sectional channels. A significant challenge of this configuration is how to get a homogeneous pressure throughout a long constricted channel; results show that the dual inlet-output gas flow circuit was able to achieve the constancy needed for a satisfactory film. Analyses of the sample films confirm acceptable uniformity even in the pressure region of 600 mTorr. Further work has shown that the glow discharge can be maintained into a pressure regime of greater than 10 Torr.

11:40am **PS2+TF-WeM12 3D Plasma Simulations of a High Density Plasma CVD Reactor using VIZGLOW**, ***P. Kothnur***, *R. Kinder*, Novellus Systems, Inc., *X. Yuan*, Esgee Technologies, Inc., *L. Raja*, The University of Texas at Austin

High-density plasma CVD (HDP-CVD) reactors are used to provide void-free gap fill of high-quality dielectric films in high aspect ratio device structures. The ability to accurately model a prototype or development design is a necessary capability of any equipment manufacturer in order to lower cost and shorten design cycle times. However, the ability to model an HDP-CVD tool accurately remains a difficult challenge due to the complex coupling of power deposition and plasma transport in a CVD chamber. To investigate issues related to power deposition and electron transport, we have used the VIZGLOW simulation software developed at Esgee Technologies to simulate 3D geometries. The simulation software enables the solution of the energy equation for electron temperature, while solving for the electron density and electrostatic fields through a quasi-neutrality condition. Electron heating is produced by electromagnetic fields, while the energy equation is solved for all heavy species. The HDP-CVD tool considered is a hemispherical inductively coupled plasma (ICP) source. The simulation results are compared to previously published experimental measurements with Langmuir probes, voltage and current monitors, optical emission spectroscopy, ion mass spectrometry, and gas quadrapole mass spectrometry. Furthermore, results from VIZGLOW are benchmarked against simulation results obtained from the Hybrid Plasma Equipment Model (HPEM). Results for experimentally measured process gases (Ar, Ar/O_2, $Ar/O_2/H_2$) at low pressures (< 15 mTorr), operating at 3-6 kW's of input power, and varying rf frequency (400 kHz –13 MHz) are discussed.

Surface Science
Room: M - Session SS1-WeM

Water/Surface Interactions & Environmental Chemistry I
Moderator: D.R. Strongin, Temple University

8:00am **SS1-WeM1 Scanning Probe Microscopy of Interfacial Water Confined Between Silica Surfaces**, ***B.I. Kim***, *J.R. Bonander, E.J. Kim, T. Tran*, Boise State University

Scanning probe microscope (SPM) techniques are employed to study the structure and mechanical properties of water confined between two silica surfaces. Water molecules adjacent to other materials, such as in the vicinity of biological cell membranes, rearrange to form "interfacial water." The interfacial water behaves differently from bulk water to a substantial degree in its structure and mechanical properties. Probing the structure of interfacial water and its mechanical properties is crucial from understanding of the biomolecular functions to the micro-machine development. Even with such importance, however, the interfacial water is difficult to observe with ordinary analytic techniques because of its delicate nature near the surface. The SPM's excellent distance and force control capability allows for investigating the interfacial water near the sample surface. A cantilever based optical interfacial force microscope (COIFM), a newly developed SPM technique at Boise State University, was used to probe the ordered structure of the interfacial water in the direction perpendicular to the surface. A Non-Contact (NC) AFM was used to image the arrangement of the interfacial water in the direction parallel to the surface. The COIFM and NC-AFM measurements were performed on silica surfaces, the most abundant substance on the earth's crust, for various relative humidity. The COIFM data show periodic features as the tip approaches the surface, showing single water-layer ordering effect of the interfacial water. In each layered region, the force decreases nonlinearly as the gap decreases. The NC-AFM images show that some water bundles lay down and some stand up, supporting the COIFM data. The humidity dependent data shows how the structure of water evolves as the thickness of the water film changes from droplets to monolayers to multilayers on the silica surface. The origin of the observed structure of the interfacial water is discussed with a simple two-dimensional self-assembly theory.

8:20am **SS1-WeM2 Theory of Tip-Sample Interaction Force for AFM in Water**, ***M. Tsukada***, Tohoku University, Japan

Noncontact AFM(ncAFM) in aqueous condition is an important method for imaging soft biological nano materials as protein. We are attempting theoretical simulation for the atomic force microscopy(AFM) in water[1,2]. So far we found various remarkable features of tip-surface interaction force mediated by water molecules[2]. They are obtained either by the molecular dynamics (MD) calculation or by the 3D-RISM (Reference Interacting Site Model) calculation.

As an example of the numerical simulation by MD method, AFM images and 3D force map of mica surface in water were calculated and compared with the experiments by Yamada's Group. The oscillatory layer structures of water exist around the interface tracing the nano-scale shapes of the sample. The phase and the amplitude of the force oscillation felt by the tip are remarkably changed depending on the lateral tip position, resuting a complicated network structure of the 3D force map. The number of the water layers in the narrow gap between the tip and sample decreased abruptly and finally disappears when the tip approaches to the surface.

The 3D-RISM method was applied to clarify the local charge separation effect on the interaction force in water. The distribution of water molecules around the atomically charged portion on the substrate is significantly disturbed, and this effect is observed in the 3D-force map from much far region as compared with that in vacuum. We discuss how drastically different the water mediated tip-sample force compared with that in vacuum, and how they influence on the images.

[1]M. Tsukada, N. Watanabe, Jpn.J.Appl.Phys., vol.48 No.3 2009

[2] Tsukada, Tagami , Phys. Rev. B submitted.

8:40am **SS1-WeM3 Isolated Single Water Molecules on Ultrathin MgO Film Studied by Scanning Tunneling Microscope**, ***H.-J. Shin****, J. Jung, K. Motobayashi,* RIKEN and University of Tokyo, Japan*, Y. Kim,* RIKEN, Japan*, M. Kawai*, RIKEN and University of Tokyo, Japan

The interaction of water molecules with solid surfaces has been a subject of considerable interests, due to its importance in the fields from atmospheric and environmental phenomena to biology, catalysis and electrochemistry [1-2]. Among various kinds of surfaces, a lot of theoretical and experimental studies have been performed regarding water on MgO(100), however, to date, there has been no direct observation of water molecules on MgO by scanning tunneling microscope (STM) as compared with those on metal surface. Here, we will present the direct observation and manipulation of single water molecules on ultrathin MgO(100) films using low-temperature scanning tunneling microscope (LT-STM). Our results rationalize the previous theoretical predictions of isolated water molecules on MgO including the optimum adsorption sites and non-dissociative adsorption of water. Moreover, we were able to dissociate a water molecule by exciting the vibrational mode of water, which is unattainable on metal surfaces. The enhanced residual time of tunneling electrons in molecules on the insulating film is responsible for this unique pathway toward dissociation of water.

[1] P. A. Thiel and T. E. Madey *Surf. Sci. Rep.* **7**, 211 (1987).

[2] M. A. Henderson, *Surf. Sci. Rep.* **46**, 5 (2002).

9:00am **SS1-WeM4 In Situ XPS Study of H_2O and CO_2 Adsorption on MgO(100) Films under Ambient Conditions**, ***J. Newberg****, D. Starr, E. Mysak,* Lawrence Berkeley National Lab*, S. Yamamoto, S. Kaya,* Stanford Synchrotron Radiation Lab*, T. Kendelewicz,* Stanford University*, S. Porsgaard, M. Salmeron,* Lawrence Berkeley National Lab*, G. Brown, Jr.,* Stanford University*, A. Nilsson,* Stanford Synchrotron Radiation Lab*, H. Bluhm*, Lawrence Berkeley National Lab

Under ambient relative humidity (RH) conditions thin film water coats metals, insulators, semiconductors and ice surfaces [1]. The water-oxide interface plays an important role in chemical, biological and industrial systems [2]. Water on MgO(100) is one of the most widely studied systems, both theoretically and experimentally, due to the simple rock salt cubic structure of MgO. Carbon dioxide is an important greenhouse gas, and the carbonation of MgO in mineral deposits has been suggested as a potential medium for carbon dioxide sequestration [3]. Here we present results from the investigation of the interaction of water and carbon dioxide with MgO(100)/Ag(100) films using the ambient pressure photoemission spectroscopy (APPES) setup at beamline 11.0.2 of the Advanced Light Source at Lawrence Berkeley National Laboratory [4]. With APPES we can quantitatively probe on a molecular level the chemical changes of the MgO(100) surface using XPS and NEXAFS while in equilibrium with water and/or carbon dioxide gases. Using 0.5 Torr isobars, we have characterized the uptake of water on MgO surfaces up to 20% RH. At roughly 0.1% RH, the MgO surface is fully hydroxylated with a ML of OH and sub-ML molecular water. At 20% RH there is roughly 1 ML of molecular water interacting with a fully hydroxylated MgO surface. Preliminary results for carbon dioxide reactivity with MgO to form carbonate showed dependency on whether the MgO surface was dry (oxide terminated) or wet (hydroxyl/water terminated). Thus, the presence of thin film water influences carbon sequestration. Ongoing studies are addressing the influences of changing RH on MgO carbonation.

References

[1] G.E Ewing 2006 Chem Rev. 106 1511.

[2] G.E. Brown et al. 1999 Chem. Rev. 99 77.

[3] T. Koljonen et al. 2004 Energy 29 1521.

[4] H. Bluhm et al. 2007 MRS Bulletin 34 1022.

9:20am **SS1-WeM5 Oxide and Carbonate Surfaces in Dynamic Equilibrium with Water Vapor**, ***V. Grassian***, University of Iowa **INVITED**

Adsorbed water plays an important role in a wide range of surface phenomena. In this talk, the focus is on water interactions with oxide and carbonate surfaces in dynamic equilibrium with water vapor under ambient conditions of temperature and relative humidity. The coverage and nature of the adsorbed water layer as a function of relative humidity are investigated. Both experiment and theory show that the adsorbed water layer is inhomogeneous and the surface is not uniformly covered even at high relative humidity. The impact of the nature of the adsorbed water layer on the surface chemistry of carbonate and oxide surfaces under ambient conditions will be discussed.

10:40am **SS1-WeM9 The Composition of the Liquid/Vapor Interface of Aqueous Nitrate and Nitric Acid Solutions**, ***T.L. Lewis***, Univ. of California, Irvine*, M.A. Brown,* Fritz-Haber-Institut der Max-Planck-Gesellschaft, Germany*, K. Callahan,* Univ. of California, Irvine*, M. Faubel,* Max-Planck-Institut für Dynamik und Selbstorganisation, Germany*, D. Tobias,* Univ. of California, Irvine*, B. Winter,* Hemholtz-Zentrum Berlin für Materialien und Energie, Germany*, J.C. Hemminger*, Univ. of California, Irvine

Nitrate anions become incorporated into sea salt aerosols through the uptake of gas-phase nitric acid in atmospheric aging processes. It has been suggested that photochemical decomposition of nitrate ions in the near surface region of such aerosols leads to OH radical production and subsequent halogen oxidation. However, the concentration of nitrate ions at the surface of aqueous solutions has been a controversial topic in the literature. We obtain a depth profile of the interfacial composition of nitrate anions in aqueous solution in the presence of alkali halide salts. All experiments were performed with XPS on a liquid micro jet and were acquired using tunable synchrotron radiation from the U41-PGM undulator beamline of the BESSY facility in Berlin, where we can vary the photoelectron kinetic energy to obtain depth dependent composition information. Our previous work shows that while nitrate and nitrite anions have a finite concentration at the interface, both prefer bulk solvation. Current results indicate that co-dissolved alkali halide salts in a sodium nitrate solution push the nitrate anion further into the bulk and away from the liquid-vapor interface. A greater effect is seen with increasing concentration of alkali halide as well as increasing size and polarizability of the halide anion. Comparison will be made with MD simulations of the corresponding solutions. In studies of nitric acid, another key component in the atmospheric chemistry of sea salt aerosols, tunable XPS elucidates the depth dependence of undissociated nitric acid. Results show that a higher concentration of undissociated nitric acid is present in the surface region relative to the bulk. Additionally, the relative concentration of undissociated nitric acid increases with increasing nitric acid concentration. These results have significant implications for the chemistry and photochemistry of sea salt aerosols.

11:00am **SS1-WeM10 Investigation of Hydroxyl Dimer Rows Formed by Thermal Dissociation of Water on Cu(110) Surface**, ***B.Y. Choi****, Y. Shi, M. Salmeron*, Lawrence Berkeley National Laboratory

Water dissociation on the surface is the first step in many reactions and wetting processes. A fundamental understanding of this process is necessary and applies to various fields, such as corrosion, catalysis, electrochemistry and hydrogen generation. Thermally dissociated water molecules on an oxygen precovered Cu(110) surface are investigated using scanning tunneling microscopy (STM) at low temperature. Chain structures of elongated molecules are obtained by dosing water on an oxygen precovered Cu(110) at 77K followed by annealing to ~180K. Density functional theory calculations reveal that the elongated molecular shapes are made of two hydrogen bonded OH molecules which form a dimer by tilting one OH to the other[1]. The weak interaction between dimers gives rise to the changes in shape of the cluster. We propose that this structural variation is the result of molecular fluctuations and from the interaction with atomic hydrogen produced by water dissociation. Switching between the different dimer shapes can be accomplished by exciting the OH-stretch mode with tunneling electrons.

[1] T. Kumagai et. al Phys. Rev. B 79, 035423 (2009)

11:20am **SS1-WeM11 Key Processes of Ice-Multilayer Evolution during Growth and Annealing Studied with STM**, ***K. Thürmer***, *S. Nie, N.C. Bartelt*, Sandia National Laboratories

Although extensive research has been aimed at the structure of ice films [1], important details of the morphology evolution, especially for films in the nm-thickness range, have remained elusive. Our capability to image up to 30 molecular layers of ice with STM [2], enables us to track the film evolution during growth and annealing. In particular, we investigate the role of new-layer nucleation and surface self-diffusion.

As reported before by others, we observe that water deposited onto Pt(111) below 120K forms amorphous films, whereas metastable cubic ice appears between 120K and ~150K. At 140K and a mean film thickness of ~1nm the film consists of 2-3 nm high crystallites, embedded in a one bilayer high wetting layer. Analyzing the annealing behavior of these crystallites we find [3] that the rate at which new layers nucleate, and not surface diffusion, determines how fast individual crystallites equilibrate. The resistance to nucleate new layers even during deposition has a surprising effect on thicker films: The deposited water attaches preferentially to growth spirals around screw dislocations, promoting the formation of metastable cubic ice [2].

Finally, we report the first measurements of surface self-diffusion on ice. Using uniform 5-nm-thick ice films (grown at 145K) as templates, we deposited a fraction of a monolayer of water at 115K to create metastable arrays of 2D-islands. By quantifying the Ostwald ripening of these arrays upon annealing between 115 and 135 K, we extract temperature-dependent diffusion rates and determine the activation energy for surface self-diffusion to be (0.4+-0.1) eV [4].

[1] A. Verdaguer, G. M. Sacha, H. Bluhm, and M. Salmeron, Chem. Rev. **106**, 1478 (2006).

[2] K. Thürmer and N. C. Bartelt, Phys. Rev. B **77**, 195425 (2008).

[3] K. Thürmer and N. C. Bartelt, Phys. Rev. Lett. **100**, 186101 (2008).

[4] S. Nie, N. C. Bartelt, and K. Thürmer, Phys. Rev. Lett. **102**, 136101 (2009).

11:40am **SS1-WeM12 Structure of Ultra Thin Water Films on Ruthenium**, ***S. Maier***, *I. Stass*, Lawrence Berkeley National Laboratory, *J.I. Cerda*, Instituto de Ciencia de Materiales de Madrid, Spain, *P.J. Feibelman*, Sandia National Laboratories, *M. Salmeron*, Lawrence Berkeley National Laboratory

The structure and chemistry of water at surfaces and interfaces is an unresolved and fundamental topic in many areas of science and technology such as catalysis, electrochemistry and environmental sciences. We use low temperature scanning tunneling microscopy in combination with DFT calculations to study the structure and reactions of ultra thin water films on Ru(0001) at the molecular scale.

We present new results on the formation of mixed water-hydroxyl structures following partial dissociation, observed above 130K. We found that the hydrogen produced during partial dissociation can be trapped in the interior of the hexagonal unit cell of the water hydroxyl structures and outside of the hexagons which is thermodynamically more stable. In addition, we studied the structure of water beyond the first layer and discovered that the hexagonal network of the second layer is surprisingly rotated 30° with respect to the first on Ru(0001) as well as on Pd(111). This rotation leads to a bonding structure between the water layers that significantly deviates from the conventional ice-like water model on hexagonal metals. We propose models for this novel structure of the first two water layers based on DFT calculations. Beyond the second water layer, a transition to the growth of compact ice clusters was found.

Surface Science
Room: N - Session SS2-WeM

Surface Chemistry and Dynamics
Moderator: C.E. Sykes, Tufts University

8:00am **SS2-WeM1 Adsorption of Xenon on Vicinal Copper Surfaces**, ***B. Holsclaw***, *A.J. Gellman*, Carnegie Mellon University

The adsorption of xenon was studied on Cu(111), Cu(221), Cu(643), and Cu(653) using temperature programmed desorption (TPD) of xenon and ultraviolet photoemission of adsorbed xenon (PAX). These experiments were performed to study the atomic and electronic structure of step-kinked, chiral copper surfaces. Xenon TPD and PAX were performed in an attempt to distinguish terrace, step-edge, and kink adsorption sites by adsorption energy (TPD) and local work function differences (PAX). The different adsorption sites could not be clearly differentiated using xenon TPD due to the complex behavior of xenon on these surfaces. Comparison of TPD spectra of *R*-3-methylcyclohexanone (R-3-MCHO) previously performed[1] on stepped and kinked copper surfaces suggests clear differences between Cu(643) and Cu(653) that are not apparent using xenon TPD. However, unique features of xenon adsorption on different copper surfaces were visually and numerically distinguishable using the PAX method. The PAX experiments on the copper surfaces demonstrate local work function differences between kink and step surface sites as well as step and terrace sites. A data fitting model was developed to analyze the PAX data for all four copper surfaces simultaneously. Kink sites were found to have a lower local work function than step sites, and steps, in turn, had a lower local work function than terrace sites. Step/kink adsorption of xenon is favored (for all surfaces studied at 50-70 K) at low coverages of xenon, but these sites do not saturate until monolayer coverage is reached. The results of this research provide several observations regarding the adsorptive behavior of xenon on vicinal copper surfaces.

[1] Horvath, J. D.; Koritnik, A.; Kamakoti, P.; Sholl, D. S.; Gellman, A. J., Enantioselective separation on a naturally chiral surface. *Journal of the American Chemical Society* **2004,** 126, (45), 14988-14994.

8:20am **SS2-WeM2 Effect of Surface Order and Thickness on the Adsorption Mechanism of NO on FePc**, ***S.R. Bishop***, *N. Tran, A.C. Kummel*, University of California, San Diego

The diverse electronic properties, chemical and thermal robustness, and ease of deposition (spin coating and organic molecular beam epitaxy) make Metallophthalocyanine (MPc) materials an attractive and economical candidate for use in chemical sensors. The purpose of this study is to obtain an atomic level understanding of the fundamental mechanisms in which analytes interact with MPc thin films. MPc thin films investigated include ordered monolayer FePc, ordered multilayer FePc, and quasi-amorphous tetra-*t*-butyl FePc multilayer thin films. These experiments were further supported with density functional theory (DFT) of NO adsorption on FePc via simulated potential energy diagram. Exploration of how surface order and thickness affects NO adsorption was performed via King and Wells sticking measurements. The unique sticking profile features a sharp, downward spike, representing a short saturation time. For monolayer and ordered multilayer FePc/Au(111), NO adsorption onto FePc saturates at 3% of a monolayer suggesting that the final chemisorption site is confined to the iron metal centers. Furthermore, the saturation coverage is only 2% for the quasi-amorphous multilayer. The reduced saturation coverage in comparison to ordered FePc is attributed to the lower packing density of the tert-*t*-butyl FePc. 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. This is consistent with the NO molecule sticking onto the monolayer FePc via physisorption to the organic periphery followed by diffusion to the Fe metal center, precursor-mediated chemisorption. For the multilayer ordered flat-lying film, the sticking probabilities are greater in comparison to the monolayer for the same incident beam energy and surface temperature. More efficient trapping onto the ordered multilayer film is consistent with NO having improved mass-matching with the multilayer FePc surface compared to monolayer. In addition, computations suggest that there are multiple available physisorption sites available within the organic periphery of the FePc films. The results strongly suggest the analyte adsorbs via a multiple pathway precursor-mediated chemisorption mechanism. A current study focuses on the analyte adsorption onto a totally amorphous film. MPc forms a β-polymorph on SiO_2 substrates which are no longer flat-lying, and planned sticking measurements of NO interaction with amorphous FePc will complete the study of the effect of surface order on analyte adsorption.

8:40am **SS2-WeM3 Interfacial Bonding of Thiophene and Aromatic Isocyanide on Au(111)**, ***J. Zhou***, *Y. Yang*, SUNY Stony Brook, *P.J. Liu, N. Camillone*, Brookhaven National Laboratory, *M. White*, Brookhaven National Laboratory & SUNY Stony Brook

The electronic structures of thiophene and 1,4-phenylene diisocyanide (PDI) adsorbed on Au(111) are investigated by two-photon photoemission (2PPE) spectroscopy and density functional theory (DFT) calculation. The adsorption of thiophene lowers the work function by 0.88 eV for Au(111) exposed to 4.0 L thiophene, due to the electron donation from the thiophene to the substrate. With thiophene adsorbed on Au(111), a localized σ^* state forms with increasing thiophene exposure on Au(111). This state is attributed to the σ^* antibonding orbital of a Au-S bond and is evidence of an orientational phase transition of adsorbed thiophene. For PDI adsorbed on Au(111), a bonding state located at 0.8 eV below the Fermi level forms at the interface. The temperature dependence of work function change of PDI/Au(111) provides an evidence for molecular crystallization on the surface. Adsorption of 1 monolayer of PDI on Au(111) lowers the work function by 0.25 eV. Upon annealing to 300 K, the work function decreases by 1.45 eV due to amplified charge transfer or dipole effects which induced by the formation of a crystallized layer.

9:00am **SS2-WeM4 Identification of C_2H_x Intermediates on Pt(111) through the Combined Use of Low Temperature Scanning Tunneling Microscopy and Reflection Absorption Infrared Spectroscopy**, *T. Okada, Y. Kim, M. Kawai,* RIKEN, Japan, ***M. Trenary***, University of Illinois at Chicago

Various C_2H_x surfaces intermediates formed through the thermal decomposition of acetylene and ethylene on the Pt(111) surface were identified and their stabilities characterized through complementary studies using the techniques of low temperature scanning tunneling microscopy (LT-STM) and reflection absorption infrared spectroscopy (RAIRS). By providing high-resolution vibrational spectra of surface species, RAIRS data is highly sensitive to the chemical identity of those species. However, it does not provide information on the relative coverages of adsorbed molecules and many important stable intermediates are invisible to RAIRS. In contrast, with a LT-STM operated at 4.7 K, individual molecules are observable and their absolute coverages are readily obtained simply by counting, yet their chemical identities cannot be directly determined from the STM images alone. In the case of acetylene, both RAIRS and LT-STM indicate that it adsorbs in a single form at low temperature in which the CC bond is positioned over a three-fold hollow site, and that the interaction with the surface occurs through both di-σ and π bonding. On warming to 250 K in the presence of coadsorbed hydrogen, RAIRS provides strong evidence for the partial hydrogenation of acetylene to form an adsorbed vinyl ($CHCH_2$) species. The LT-STM images following a 250 K anneal in the presence of coadsorbed hydrogen show a marked increase in the coverage of a species that is identified as vinyl, based on the RAIRS results. Both techniques indicate that adsorbed acetylene is stable up to 300 K. A third species, in addition to adsorbed acetylene and vinyl, is also observed with the LT-STM after a 300 K anneal, which is identified as vinylidene, CCH_2. However, the RAIRS evidence for a vinylidene species is not definitive. In the case of ethylene adsorption at low temperature, RAIRS provides clear evidence for a di-σ bonded form of ethylene at low temperatures that coverts to ethylidyne at 280-420 K. The LT-STM images show that ethylene exists in both π-bonded and di-σ bonded forms at low temperature and that the two forms can be easily interconverted using electron pulses from the STM tip. On the basis of RAIRS experiments, it was found that surface carbon formed through the complete dehydrogenation of acetylene could be hydrogenated to form ethylidyne (CCH_3), from which it was inferred that the surface carbon was in the form of C_2 molecules. A form of surface carbon that can be hydrogenated to ethylidyne was also identified with LT-STM. Other surface species that have been investigated with the two techniques include ethynyl (CCH), ethylidene ($CHCH_3$), and methylidyne (CH).

9:20am **SS2-WeM5 Dehydrogenation of Single Ammonia Molecules on Ruthenium**, ***I. Stass***, *S. Maier, M. Salmeron*, Lawrence Berkeley National Laboratory

Ammonia (NH_3) can be potentially used for hydrogen storage, because the dissociation of ammonia molecules generates hydrogen. Although Ruthenium is the best elementary metallic catalyst for ammonia synthesis, the exact reaction mechanisms at the atomic scale of both synthesis and dissociation over the Ruthenium surface have yet to be understood. Previously, the dehydrogenated products were obtained by annealing the sample and characterized by spectroscopic methods.

We studied the dehydrogenation of single ammonia molecules adsorbed on a Ru(0001) surface, by means of scanning tunneling microscopy (STM) at low temperature. The sudden change in tunneling current during the dissociation process allows us to study the dissociation mechanism and rate of single molecules in detail. We observe the different dehydrogenation steps after selectively applying voltage pulses in the order of a few volts between STM tip and an adsorbed ammonia molecule. The various dissociation products show a distinct imaging contrast. Together with the assignment of the adsorption site, this leads to the identification of the dissociation products. We will discuss to what extent electron induced and electric field driven processes, respectively, are affecting the dissociation mechanism of ammonia and its dissociation products.

9:40am **SS2-WeM6 The Ca / MEH-CN-PPV Interface: Ca Adsorption Calorimetry, LEIS and XPS**, ***J.C. Sharp***, *J.H. Baricuatro,* University of Washington, *F. Bebensee, H.-P. Steinrueck, J.M. Gottfried,* Universitaet Erlangen-Nuernberg, Germany, *C.T. Campbell*, University of Washington

Conjugated polymers are of interest for use in photovoltaics and OLEDs because of the tunability of their band gap and ease of processing them into devices. Poly(5-(2-ethylhexyloxy)-2-methoxy-cyanoterephthalylidene) (MEH-CN-PPV) has high photoluminescence efficiency and thus has potential use in OLEDs. The interaction between the conjugated polymer and metal electrode is critical to the performance of these devices. The energetics and structure of calcium growth on MEH-CN-PPV was studied using adsorption microcalorimetry and low-energy ion scattering spectroscopy (LEIS) in ultrahigh vacuum. At 300 K the integrated Ca LEIS peak area grew slowly until ~1.5 ML and the rate of growth increased until a continuous film of Ca was formed by ~15 ML. The slow initial growth rate is due to calcium diffusing subsurface. After ~1.5 ML, Ca forms 3-D islands on the surface. At 130 K, the transitions from subsurface diffusion to 3D cluster growth to film formation occur at lower coverages. The initial heat of adsorption of Ca on MEH-CN-PPV at 300 K is 436 kJ/mol. The heat of adsorption increases to 464 kJ/mol at ~0.1 ML and then decreases to the heat of sublimation of Ca by 4 ML. Similar behavior is seen at 130 K with the initial heat of adsorption being 326 kJ/mol and increasing to 331 kJ/mol at ~0.1 ML and decreasing to the heat of sublimation already by 1.25 ML. The sticking probability (S) at 300 K was 0.70 initially and increased to 0.75 at ~0.1 ML of Ca coverage. After ~0.1 ML, S decreased to 0.64 by ~1.5 ML, then gradually increases to unity. The initial sticking probability at 130 K was 0.92 and increased toward unity. The thermodynamic, sticking and growth behavior below 1.5 ML, where Ca is interacting strongly with specific adsorption sites on the polymer, will be discussed

10:40am **SS2-WeM9 STM Tip Induced Surface Reactions on TiO_2(110)**, ***D.V. Potapenko***, *R.M. Osgood*, Columbia University

Chemistry on the surfaces of photocatalytic materials, including TiO_2, is driven by the charge carriers that are created in the bulk of the catalyst by light adsorption. The tip of a scanning tunneling microscope may serve as an alternative source of both free electrons and holes in a semiconductor. We have studied adsorption and tip-induced surface chemistry of 4-bromobiphenyl on the TiO_2(110) surface. The adsorbed molecules could be identified in the STM images at the limit of low coverages. The response of the surface to the adsorbed substance was characterized with in situ temperature program desorption. Passing the electric current from the STM tip through molecules caused dissociation of the molecules as was indicated by the changes in the STM images. We report on the conditions of the tip-induced chemistry and propose mechanistic explanation of the observed phenomena. An important follow on experiment to this work will be to examine reactions on nanocrystal TiO_2.

11:00am **SS2-WeM10 H_2O Interaction with Oxygen Adatoms on TiO_2(110)**, ***Y. Du***, *A. Deskins, Z. Zhang, Z. Dohnalek, M. Dupuis, I. Lyubinetsky*, Pacific Northwest National Laboratory

Water and oxygen interactions on the catalytically important TiO_2 surfaces have attracted great interest from both fundamental and technological points of view. In this work, surface chemistry of water on oxidized TiO_2(110) surfaces is investigated by scanning tunneling microscopy studies and density functional theory calculations. We show that oxygen adatoms (O_a), generated during oxygen dissociation, alter the water dissociation and recombination chemistry through two distinctive pathways. Depending on whether H_2O and O_a are on the same or adjacent Ti^{4+} rows, O_a facilitates H_2O dissociation and proton transfer to form a terminal hydroxyl pair, positioned along or across the Ti^{4+} row, respectively. The latter process involves proton transfer through a bridging oxygen atom where H_2O is considered to be in a ''pseudo-dissociated'' state. In both pathways, the reverse H transfer results in H_2O reformation and statistical O scrambling, as manifested by an apparent along- or across-row motion of O_a's.

11:20am **SS2-WeM11 Sulfur Adsorption on Ag(111) and Ag(100): Structures and Surface Dynamics**, ***D.-J. Liu***, *M. Shen, S. Russel, C.J. Jenks, J.W. Evans, P.A. Thiel*, Iowa State University

Exposure to sulfur (S) of Ag(111) and Ag(100) produces ordered surface structures as observed by STM. On Ag(111), a self-organized dot-row structure forms at around 200 K [1]. The dots, likely Ag_3S_3 clusters, can rearrange and form other more closed-packed structures at higher S coverages. On Ag(100) at 230 K, a $\sqrt{17}$ reconstruction structure appears for S coverage above 0.25 ML, together with a p(2x2) structure. STM studies also reveal that exposure to sulfur generally accelerates coarsening of 2D Ag nanoislands preformed on the surface by Ag deposition. For Ag(111), since steps serve as sinks for S, dramatic enhancement of Ostwald ripening only occurs above a threshold (step saturation) coverage of S [2]. For Ag(100), Ostwald ripening is activated with a rate increasing gradually with increasing S coverage. Possible acceleration mechanisms include AgnSm complex mediated mass transport, or S-catalyzed attachment-detachment. We perform a detailed analysis of the stability and formation energies of various structures and Ag-S complexes using DFT. Many aspects of the observed structures and mechanisms for mass transport during coarsening are elucidated based on these DFT energetics together with kinetic modeling.

[1] Shen *et al*. J. Phys. Chem. C **112** (2008) 4281

[2] Shen *et al*. J. Chem. Phys. **130** (2009) 094701

11:40am **SS2-WeM12 Ionicity of Adsorbates: Dependence on Coverage, Site, and Substrate**, ***P.S. Bagus***, University of North Texas, *Ch. Wöll*, Ruhr-Universitaet Bochum, Germany, *A. Wieckowski*, University of Illinois at Urbana-Champaign

We present detailed theoretical analyses of nominally anionic Iodine and nominally cationic Cs adsorbed on Cu(111) and Pt(111) surfaces. We consider the consequences of the coverage, the choice of on-top or three-fold sites, and the differences between Cu and Pt substrates on the degree of ionicity and on other properties of the interaction. This work extends our earlier studies of I and Cs on Cu(111)[1] and of I/Pt(111).[2] There we demonstrated that, although both Cs and I were dominantly ionic adsorbates, the properties of the adsorption, including work function changes, $\Delta\Phi$, and photoemission binding energy shifts, ΔBE, depended on other factors besides the adsorbate ionicity. However in this earlier work, only a single I or Cs adsorbate was explicitly treated and we neglected both direct and indirect, substrate mediated, adsorbate-adsorbate interactions. Now, we use models where several adsorbates are included, thus explicitly modeling lower and higher coverages. In particular, we examine whether the coverage dependent departures from ideal ionicity are different for cations and anions. Furthermore, we examine how $\Delta\Phi$ depends on the adsorbate-adsorbate interaction and compare our predictions with measurements of $\Delta\Phi$ as a function of coverage. This is relevant for the modification of charge transport barriers, which is key for the design of organic electronics.[3] The distance of I above Pt(111) is quite different for on-top and three-fold sites,[2] which has important consequences for $\Delta\Phi$ and ΔBE. Here, we examine the generality of different heights of ionic adsorbates at these sites and how this difference is affected by the sign of the ionicity and the substrate. Our theoretical methodology uses wavefunctions for cluster models of the surface since this allows us to determine the quantitative importance of the individual physical and chemical mechanisms that contribute to the interaction. Our present work marks the first time that these methods have been applied to study the influence of coverage for halogen and alkali metal adsorbates.

[1] P. S. Bagus, D. Käfer, G. Witte, and C.Wöll, Phys. Rev. Lett., **100**, 126101 (2008).

[2] P. S. Bagus, C. Wöll, and A. Wieckowski, Surf. Sci. **603**, 273 (2009).

[3] G. Witte, S. Lukas, P. S. Bagus, and C. Wöll, Appl. Phys. Lett., **87**,263502 (2005).

Thin Film
Room: B4 - Session TF-WeM

Nanostructuring Thin Films I
Moderator: A.V. Melechko, North Carolina State University

8:00am **TF-WeM1 Growth of Thin Films of Nanomeshes on Solid Surfaces through Self-Assembly**, ***F. Tao***, *S. Bernasek*, Princeton University

The growth of homogeneous 2-D multi-component ordered thin films has attracted surprising interest because they may offer the multiple functions of organic materials and the flexibility in fine-tuning the chemical, physical and mechanical properties for desirable needs in a wide spectrum of technological areas. Controllable molecular self-assembly on solid surfaces is a promising approach to the design of such thin films. Coadsorbed monolayers of 5-octadecyloxyisophthalic acid (5OIA) and octanoic acid and of 5OIA and terephthalic acid were fabricated on highly-ordered pyrolytic graphite (HOPG). The atomically-resolved morphology of these self-assembled monolayers was investigated using high-resolution scanning tunneling microscopy (STM). 5OIA coadsorbs with terephthalic acid via a hydrogen-bonding network, forming ordered domains made of alternating 5OIA and terephthalic acid lamellae. In the coadsorption of 5OIA with octanoic acid, 5OIA and octanoic acid alternately pack at the molecular level in each lamella, forming a homogeneous two-component crystal. Due to the different chain-lengths of the two components, a nano-hole with a size of 13.5 Å x 8.5 Å x 1.8 Å is formed in each lattice unit, producing homogeneous nano-meshes. The size of nano-hole in the meshes is tunable by using alkyl chain of either of the two components with different length. This coadsorbed molecule-by-molecule self-assembly is the first demonstration of an approach to fabricating multi-component 2-D crystalline thin films at the molecular level. It suggests a new strategy to precisely and controllably grow homogeneous nano-structured composite thin films.

8:20am **TF-WeM2 Nanometer-Scale Direct-Write 3D-Patterning using Probes**, ***A.W. Knoll***, *D. Pires, U. Drechsler*, IBM Zurich Research Laboratory, Switzerland, *J.L. Hedrick*, IBM Almaden Research Center, *M. Despont, U.T. Duerig*, IBM Zurich Research Laboratory, Switzerland

Progress in nanotechnology is intimately linked to the existence of high quality methods for producing nanoscale objects and patterns at surfaces. Scanning probe technologies are intrinsically capable of addressing real space with atomic resolution and have been used to fabricate nano-scale devices with exceptional quality. However, high resolution patterning in combination with sufficient throughput remains challenging. We have discovered that organic molecular glasses can be reproducibly removed at the micro-second time scale with nanometer scale precision using heated probes, which opens up new perspectives for nanopatterning.

In our experiments, a thin film of molecular glass with a thickness of 10-100 nm is deposited on a substrate by spin-coating or evaporation. The material is locally desorbed by heating the tip to 300-500 ºC and applying a mechanical force of 50-100 nN for a duration of 5 µs, leaving behind a well defined void. By laterally displacing the probe and repeating the process, any arbitrary pattern can be written whereby the resolution of the process is determined by the apex dimensions of the probe.

Material removal can be cumulated thereby enabling the fabrication of three-dimensional structures. A replica of the Matterhorn was fabricated by consecutive removal of molecular glass layers. The almost perfect conformal reproduction of the original proves that the final structure is a linear superposition of well defined single patterning steps.

The created two and three-dimensional structures were transferred into silicon substrates using standard RIE technology. Additionally, to enhance the aspect ratio, a three layer transfer process has been developed. It enables vertical amplification of the written structures by a factor of 50 without significant loss of lateral resolution.

Using this new technology, one is able to fabricate complex three-dimensionally textured substrates, e.g. for the guided and directed assembly of shape-matching objects. The technique also offers a competitive alternative in terms of resolution and speed to high-resolution electron beam lithography.

8:40am **TF-WeM3 Subwavelength Patterning of Organic Monolayers Via Nonlinear Laser Processing with fs-laser Pulses**, ***N.O. Hartmann***, *S. Franzka, M. Mathieu*, University of Duisburg-Essen, Germany, *J. Koch, B.N. Chichkov*, Laser Zentrum Hannover, Germany, *A. Ostendorf*, Ruhr-Universität Bochum, Germany

In the last decade, surface processing with ultra-short laser pulses has emerged as a powerful tool for nanofabrication. Here, fs-laser patterning of self-assembled organic monolayers offers a variety of particularly promising perspectives. The ultrathin nature of these coatings allows for single pulse processing and hence ensures short processing times. It also allows for well-defined irradiation and burr-free patterning of the coating and avoids bubble and particle formation. All off which are problems usually encountered in fs-laser processing. Moreover, varying the chemical structure of the monolayer provides a means to tailor cross sections, incubation effects and resist properties and to enable chemical nanopatterning. Surprisingly, despite these promising perspectives, fs-laser processing of organic monolayers still is largely unexplored. In a recent study we investigated fs-laser patterning of alkylsiloxane monolayers on quartz glass substrates at λ=800 nm and pulse lengths below 30 fs [1]. Selective decomposition of the coating with single laser pulses at subwavelength resolution can be carried out over a wide range of fluences from 4.2 down to 3.1 J/cm^2. In particular, at a 1/e laser spot diameter of 1.8 µm, structures with a width down to 250 nm and below were fabricated. Very similar results were also obtained from multiple pulse patterning experiments suggesting that incubation effects are negligible. Hence precise fabrication of complex patterns appears feasible. This opens up a facile route towards laser fabrication of transparent templates with chemical structures down into the sub 100 nm regime. Such templates represent promising platforms for biotechnological applications, e. g. biosensor arrays. Processing at higher fluences, also provides a facile route towards combined chemical/topographic structures, e. g. for microfluidic applications. With a band gap of 9 eV, quartz glass, of course, represents an ideal platform for nonlinear fs-laser processing via multiphoton absorption processes. Further results, though, demonstrate that fs-laser processing also allows for subwavelength patterning of organic monolayers on thin gold films. A general account on recent achievements in nonlinear laser patterning of organic monolayers via multiphoton absorption and photothermal processes is given.

[1] N. Hartmann, S. Franzka, J. Koch, A. Ostendorf und B. N. Chichkov, Appl. Phys. Lett. 92 (2008) 223111.

9:00am **TF-WeM4 Alloy Destabilization Behavior of Cu-Ni Thin Films on Si during Solid State Dewetting**

S. Seshabhattar, North Carolina State University*, P.D. Rack, R. Pearce,* University of Tennessee*, D.K. Hensley, M. Fuentes-Cabrera, J.D. Fowlkes,* Oak Ridge National Laboratory*, M.L. Simpson,* Oak Ridge National Laboratory and University of Tennessee*, A.V. Melechko*, North Carolina State University

Synthesis of nanoparticles research witnessed a remarkable headway with techniques spanning a wide range of materials and offering good control over particle shape and size. Top –down approaches have become successful in achieving controlled positioning of nanoparticles in pre-defined templates. A self-assembly method, however, is highly desirable because of its simplicity and compatibility with heterogeneous integration processes. Thin elemental or multicomponent films can be destabilized into self assembled arrays of nanoparticles. We will discuss how heating of ultrathin films can be a powerful but simple tool to fabricate functional nanostructures. Thin metal films on inert substrates are generally unstable, with their free energy resembling that of a spinodal system. Such films can spontaneously evolve into predictable morphologies with defined length scales. This process has been extensively used to prepare arrays of catalyst nanoparticles on Si surfaces for growth of vertically aligned carbon nanofibers. In this work we report on the behavior of Cu-Ni alloy thin films during solid state dewetting. The segregation of Cu-Ni alloy thin films during solid state destabilization on Si is in contrast to behavior expected from isomorphous system. Thin films of Cu-Ni and Ti-Cu-Ni were formed on Si and subjected to annealing temperatures from 300 º C - 700ºC. Scanning Electron Microscopy(SEM) micrographs of these films revealed the formation of Cu-rich clusters on the surface prior to complete dewetting of the film in the range of temperatures much lower than dewetting of Ni film. The size and density of the Cu-rich regions increased with the increase in annealing temperatures. With increase in temperature the shape of these regions developed from irregular to cubical. The evolution of the alloy composition studied with Energy-Dispersive X-ray spectroscopy(EDX) mapping on both Si and Si covered with a Ti diffusion barrier will be presented. The solid state dewetting will be compared to laser processed films, that is, dewetting in a fluidic transport regime rather than diffusive transport regime.

This work was sponsored by the Materials Sciences and Engineering program of the DOE Office of Science.

9:20am **TF-WeM5 Electrical, Optical and Structural Studies of Shallow Buried Au-PMMA Composite Films formed by Very Low Energy Ion Implantation**

F.S. Teixeira*, M.C. Salvadori, M. Cattani,* University of Sao Paulo, Brazil*, I.G. Brown*, Lawrence Berkeley National Laboratory

We describe our electrical, optical and structural studies of sub-nanometer composite films formed using a pulsed cathodic arc plasma gun to implant 49 eV gold ions into PMMA (polymethylmethacrylate) thin films (~ 50 nm thick). Electrical resistance measurements *in situ* as a function of implantation dose (up to 2 x 10^{16} atoms/cm^2) show a conductivity increase that is well described by the percolation theory power law $\sigma/\sigma_0 \approx (x - x_c)^t$, where σ/σ_0 is the measured metal/insulator composite conductivity ratio, x is the normalized concentration of the conducting phase atoms, x_c is the normalized critical concentration (percolation threshold) below which the composite has zero conductivity, and t is the critical exponent. For our Au/PMMA composite we found $\sigma/\sigma_0 \approx (x - 0.4)^{1.65}$, where x_c corresponds to a critical dose $\phi_c = 1.0 \times 10^{16}$ atoms/cm^2. We point out that the low energy implantation used here does not create any target vacancies or carbonization, which can occur for incident ion energy greater than about 100 eV, and thus that the electronic transport properties of the composite formed here are due only to the gold phase embedded in the original polymer. TEM (Transmission Electron Microscopy) images reveal that the gold phase is a shallow-buried sub-10 nm layer consisting of a distribution of nanoclusters (diameters ≈ 2 nm – 5 nm for implantation dose $\phi < \phi_c$), spontaneously aggregated from the implanted gold ions, evolving to larger clusters as the dose increases. The computer simulation software TRIDYN, a dynamic version of the widely used TRIM (Transport and Range of Ions in Matter) that is more suitable when compositional changes are induced by the implantation itself as is the case here, gave very good predictions for the intermixed layer width and ion range, both with values lower than 10 nm. UV-Vis optical spectroscopy (ultraviolet to visible wavelength range) of the samples showed localized plasmon surface resonance effects from gold nanoparticles. SAXS (Small Angle X-ray Scattering) analysis was used to study the fractal character of the growth dynamics, the correlation lengths, and the size of agglomerates and elementary clusters. We related SAXS and UV-Vis data to percolation electrical behaviour. Note that the entire material is composed of a sequence, from substrate to surface, of PMMA thin film, shallow-buried composite film of nanoclusters, and an ultra thin film of unaltered polymer. These three layers can be electron beam lithographed at the same time, a highly desirable feature for application of the material for organic electronics/photonics.

9:40am **TF-WeM6 Preparation and Microstructure of Silver Nanoparticles Embedded into a Flourocarbon Matrix Prepared by RF and DC Sputtering**

D.G. Vásquez Mazzoti, ***A.F. Talledo Coronado***, Universidad Nacional de Ingenieria, Peru*, C. Benndorf*, University of Hamburg, Germany

Composite materials consisting of metal nanoparticles embedded in transparent dielectric materials are interesting materials due the size effects induced by the nanoparticles. We report about the preparation of fluorocarbon thin films with embedded silver nanoparticles and their characterization with UV-VIS spectroscopy, XPS (X-ray induced photoelectron spectroscopy), IR (infrared spectroscopy) and HRTEM (high resolution transmission electron microscopy). Further, the surface free energy was determined from contact angle measurements using different liquids. The metal-dielectric nanocomposites with a layered structure were prepared by switching alternatively the substrates (glass or stainless steel) from an RF powered Teflon target towards an Ag target powered by DC. The high resolution XPS spectra from the C 1s region displayed four peaks (on stainless steal substrates) with positions of 284.5, 286.5, 288.6 and 290.7 eV, related to C-H$_x$, C-F, C-F$_2$ and C-F$_3$ bonds, respectively. For comparison, we measured the XPS spectrum from a Teflon surface (after scratching the surface). From this surface, the carbon 1 s region was dominated by two peaks, located at 284.6 (C-H$_x$) and 289.0 eV (C-F$_2$). The different composition of the sputtered films is due to the plasma process, which produces fragments like F, CF, CF$_2$ and CF$_3$ radicals and ions. The incorporated Ag nanoparticles gave only weak XPS signals from the Ag 3d doublet around 368 - 374 eV. UV-VIS spectra, measured in the range of 300 - 800 nm in transmission, showed with the presence of the Ag nanoparticles pronounced absorption peaks at around 420 to 480 nm, depending on the amount of incorporated Ag and different preparation conditions. This absorption maximum is related by us, in accordance with other authors, to the surface plasmon loss of the Ag nanoparticles where the loss energy depends on the particle size and form, the concentration of the particles and the nature (dielectric constant) of the surrounding matrix. HRTEM pictures showed the presence of Ag nanoparticles with sizes between 5 and 50 nm. The filling factor of Ag (within the fluorocarbon matrix) was about 0.3. Crystalline planes from the Ag nanoparticles could be observed with (200) and (111) orientation. The evaluation of the lattice spacing resulted in d_{200} = 0.204 and d_{111} =0. 237 nm which is within 1% of the bulk Ag values. The surface free energy of our films was determined by the observation of the contact angle of liquid drops, using water, ethyl alcohol and olive oil. The evaluation was done following the method of Zisman. We obtained a value around 15mN/m, which is approximately 50% of the value reported for bulk Teflon.

10:40am **TF-WeM9 Dewetting in Single and Bilayer Metallic Films under Pulsed Laser Irradiation**

H. Krishna, Washington University*, R. Sachan, N. Shirato, J. Strader,* University of Tennessee*, A.K. Gangopadhyay,* Washington University*, H. Garcia,* Southern Illinois University, ***R. Kalyanaraman***, University of Tennessee **INVITED**

Metallic nanostructures and nanocomposites have many applications related to their magnetic, plasmonic and magneto-optical properties. Fabricating desired structures and compositions in a reliable and cost-effective manner is therefore of substantial importance to applications in energy harvesting, sensing and data processing. Here we will focus on the robust pattern formation characteristics of thermodynamically unstable single and bilayer metallic films. The unstable energy state manifests itself as spontaneous dewetting and self-organization under energetic radiation, such as from nanosecond pulse lasers. The ensuing patterns contain a fascinating range of nanostructures as well as physical properties. The general principle that explains the length-scale selection for this pattern formation is the balance between rates of free energy change and energy loss during film deformation. We have applied this principle to the single and bilayer systems and have found very good agreement with experimental observations. We will also briefly discuss our studies of nanoscale nucleation, size-dependent magnetic anisotropy, plasmonic behavior and the magneto-optical properties of some elemental and composite metallic materials made by this self-organization process.

* This work is supported by NSF grants CAREER DMI-0449258, CMMI-0757589, DMR-0805258 and by Center for Materials Innovation grant # 94509A

11:20am **TF-WeM11 Subsurface Oxidation for Micropatterning Silicon (SOMS)**

F. Zhang, Brigham Young University*, K. Sautter,* Yield Engineering Systems*, R.C. Davis, M.R. Linford*, Brigham Young University

We introduce a straightforward patterning technique for native oxide-capped silicon to produce features of both nanometer and micron dimensions: subsurface oxidation for micropatterning silicon (SOMS). In this method, a stencil mask with, for example, ca. 5 micron features is positioned over a silicon surface. RF plasma oxidation of the substrate creates a pattern of thicker oxide in the exposed regions. Etching with HF or

KOH produces very shallow (few nanometer) or much higher aspect ratio features (hundreds of nanometers deep) on silicon, respectively, where patterning is confirmed by atomic force microscopy, scanning electron microscopy, and optical microscopy. The oxidation process itself is studied under a variety of reaction conditions, which have not been thoroughly explored in the literature, including higher and lower oxygen pressures (2 and 0.5 Torr), a variety of powers (50 – 400W), different treatment times, and as a function of reagent purity (99.5% or 99.994% oxygen). A mathematical model of the results is derived. The reagent purity, even at the high level studied, is shown to influence the process. SOMS can be easily performed in any normal chemistry lab with a plasma generator. Because of its simplicity, it may have industrial viability.

11:40am **TF-WeM12 Variable-Thickness Patterns using Full-Wafer Dynamic Stencil Lithography**, ***V. Savu***, EPFL, Switzerland, *S. Sansa, F. Perez-Murano,* CNM-IMB, CSIC, Spain, *J. Brugger*, EPFL, Switzerland

Stencil lithography is a shadow mask technique allowing patterning at full-wafer scale from micro to nanostructures by material deposition, etching or ion implantation. It offers unique opportunities for processing where standard lithography cannot be applied, such as on top of 3-dimensional and flexible/functionalized substrates [1]. In the dynamic stencil mode, the stencil and substrate move in-situ relative to each other during or in between depositions. This mode can be used for multi-material, variable thickness patterning [2]. Here we present the in-situ fabrication of variable-thickness structures by using dynamic stencil lithography.

The dynamic stencil setup consists of an x-y moving stage with 20 nm encoding resolution each and three z-stages on which the stencil is attached, and a fixed part which holds the substrate, as described in [3]. The x-y stage is programmed to move along various trajectories. The movement parameters are the (x,y) coordinates of the start and end point (corners), the gap between stencil and substrate, and the stencil speed (0.04-5 µm/s).

By evaporating materials at a constant rate while changing the speed of the stencil, we obtained variable-height structures. We also varied substrate materials (SiO_2, SiN) and parameters such as the deposition rate and the stencil-substrate gap. These structures were characterized by scanning electron microscopy and atomic force microscopy. We also analyzed the pattern transfer integrity from the stencil to the substrate as a function of stencil-substrate gap and aperture size.

Dynamic stencils are used here for patterning two-dimensional variable-height structures by material deposition through a stencil at 4” wafer scale. The contamination-free, parallel-processing, and versatile nature of dynamic stencil lithography provides custom applications with a novel solution.

[1] K. Sidler, O. Vazquez-Mena, V. Savu, G. Villanueva, M. A. F. van den Boogaart, and J. Brugger, "Resistivity measurements of gold wires fabricated by stencil lithography on flexible polymer substrates," *Microelectronic Engineering,* vol. 85, pp. 1108-1111, May-Jun 2008.

[2] J. L. Wasserman, K. Lucas, S. H. Lee, A. Ashton, C. T. Crowl, and N. Markovic, "Fabrication of one-dimensional programmable-height nanostructures via dynamic stencil deposition," *Review of Scientific Instruments,* vol. 79, p. 4, Jul 2008.

[3] V. Savu, M. A. F. v. d. Boogaart, J. Brugger, J. Arcamone, M. Sansa, and F. Perez-Murano, "Dynamic stencil lithography on full wafer scale," *Journal of Vacuum Science & Technology B,* vol. 26, pp. 2054-2058, 2008.

Tribology Focus Topic
Room: C4 - Session TR+NS-WeM

Nanomechanics and Nanotribology
Moderator: C.M. Mate, Hitachi San Jose Research Center

8:00am **TR+NS-WeM1 Nonlinear Contact Area Dependence of Sliding Friction for Metallic Nanoparticles**, ***D. Dietzel***, *T. Moenninghoff, A. Schirmeisen*, University of Münster, Germany

The existence of superlow friction under appropriate interface conditions is one of the most intriguing concepts in nanotribology. If an interface between two incommensurate surfaces is atomically clean, a state of virtually frictionless sliding is anticipated, often referred to as ‘superlubricity’ or ‘structural lubricity’. But although superlubricity is a widely accepted theoretical concept, an unambiguous and direct verification has been difficult in the past. Theory predicts that the lattice mismatch at the interface causes a decrease of the potential barrier between stable states with increasing contact size that ultimately leads to vanishing friction. Therefore, analyzing the contact area dependence of superlubric friction might be a straightforward approach to confirm the frictional conditions. Unfortunately, conventional friction force microscopy (FFM) has limitations inherent to the experimental configuration when it comes to contact area dependent measurements: Apart from the rather limited variety of material combinations, the fixed tip radius makes it especially difficult to analyze effects as a function of the contact area. In order to analyze the contact area dependence of interfacial friction, the friction between two objects in relative motion with a well-defined contact area should be measured instead of the friction between tip and surface. Therefore we have manipulated nanometer scale metallic particles on atomically flat surfaces by contact mode atomic force microscopy techniques and quantitative information on interfacial friction has been extracted from the lateral manipulation of these nanoparticles[1]. In previous experiments[2] we found two distinct frictional states during particle sliding of Sb-particles on HOPG substrate: Some particles show finite friction increasing linearly with interface area, thus reinforcing Amonton’s law at the nanoscale, other particles assume a state of frictionless or ‘superlubric’ sliding.

In this contribution we show new measurements which were concentrated on the particles exhibiting vanishing friction. By optimizing our experimental sensitivity we succeeded for the first time to analyze the contact area dependence of friction force of these low friction particles. In contrast to the ‘Amonton’-like particles, interfacial friction of the low friction particles showed strongly nonlinear contact area dependence. The experimental results are compared to theoretical considerations, which predict that the shear stress of sliding superlubric particles should decrease with increasing particle size.

[1] Dietzel et al., J. Appl. Phys.102, 084306 (2007).

[2] Dietzel et al., Phys. Rev. Lett. 101, 125505 (2008).

8:20am **TR+NS-WeM2 Why is Graphite so Slippery? Gathering Clues from Atomically Resolved Three-Dimensional Lateral Force Measurements**, ***M.Z. Baykara***, *T.C. Schwendemann, B.J. Albers, N. Pilet, E.I. Altman, U.D. Schwarz*, Yale University

Conventional lateral force experiments give insufficient insight into the fundamental reasons for graphite’s outstanding qualities as a solid lubricant due to an averaging effect caused by the finite contact area of the tip with the sample. To overcome this limitation, we used a noncontact atomic force microscopy-based approach that enables use of atomically sharp tips. The new technique [1], performed using a home-built low temperature, ultrahigh vacuum atomic force microscope [2], allows the measurement of normal and lateral surface forces in a dense three-dimensional raster with picometer and piconewton resolution.

In this presentation, we analyze the height and lattice site dependence of lateral forces, their dependence on normal load, and the effect of tip shape in detail. The lateral forces are found to be heavily concentrated in the hollow sites of the graphite lattice, surrounded by a *matrix* of vanishingly small lateral forces. It will be argued that this astonishing localization may be a reason for graphite’s excellent lubrication properties. In addition, the distance and load dependence of the lateral forces experienced along possible “escape routes” from the hollow sites, which would be followed by a slider that is dragged out of them, are studied. Surprisingly, the maximum lateral forces along these escape routes, which ultimately determine the static friction, are found to depend linearly on normal load, suggesting the validity of Amontons' law in the noncontact regime.

[1] B. J. Albers *et al.*, Nature Nanotechnology **4**, 307 (2009).

[2] B. J. Albers *et al.*, Rev. Sci Instrum. **79**, 033704 (2008).

8:40am **TR+NS-WeM3 Atomistic Simulations of Friction and Wear of Carbon-Based Materials**, ***I. Szlufarska***, *Y. Mo, M. Mishra*, University of Wisconsin, Madison **INVITED**

Controlling tribological properties requires understanding a bewildering array of interrelated mechanisms, including elastic instabilities, plastic deformation, fracture, and chemical reactions. Large scale atomistic simulations have been used to unravel some of these mechanisms. Tribological studies are typically divided into a wearless regime, where deformation is primarily elastic, and a wear regime where permanent deformation occurs. For wearless contacts, I will discuss the breakdown of continuum mechanics at the nanoscale and present our recent discovery of friction laws in dry nanoscale contacts. This discovery lays a foundation for unified friction laws across all length scales. In the wear regime I will focus on the origins of recently observed ductile wear in nominally brittle SiC. Although this ductile wear holds potential for greatly enhancing the ease of machining of high-performance ceramics, its origin is still an open question. I will evaluate potential mechanisms for ductile wear, including the possibility of transformation to more ductile phases, dislocation mediated plasticity, and nanoindentation-induced amorphization.

9:20am **TR+NS-WeM5 MD and AFM Studies of the Adhesion of Diamond, Silicon, and UNCD**, ***J.A. Harrison***, *P.L. Piotrowski, G.T. Gao,* United States Naval Academy*, R.J. Cannara,* National Institute of Standards and Technology*, R.W. Carpick*, University of Pennsylvania

For the past several years, we have used molecular dynamics (MD) simulations and classical reactive empirical bond-order (REBO and AIREBO) potentials to elucidate the atomic-scale mechanisms of friction and adhesion in solid lubricants. Recently, we have conducted complementary MD and atomic force microscopy (AFM) examinations of adhesion and atomic-scale friction for diamond, silicon, and nanocrystalline diamond interfaces. These materials are highly relevant to micro- and nano-electromechanical systems (M/NEMS), nanomanufacturing, and a host of other applications. The conditions of the simulations and the experiments were designed to correspond as closely as the methods allow. The effects of variables including diamond (or silicon) crystal orientation, hydrogen termination, temperature, and roughness on adhesion and friction can all be examined. In this talk, we will discuss our most recent results which highlight atomic mechanisms of friction and adhesion as well as the limits of continuum mechanics.

*JAH acknowledges support from The Air Force Office of Scientific Research (AFSOR) as part of the Extreme Friction MURI and from The Office of Naval Research. JAH & RWC also acknowledge support from AFOSR's Aerospace, Chemical, and Material Sciences Directorate.

9:40am **TR+NS-WeM6 Which Fractal Parameter Most Determines Adhesion?***, D. Liu,* Worcester Polytechnic Institute*, J. Martin,* Analog Devices, Inc.*, **N.A. Burnham***, Worcester Polytechnic Institute

The topography of a surface can be characterized by three fractal parameters: its surface roughness, its roughness exponent, and its lateral correlation length [1]. In 2001, T.S. Chow [2] predicted that a decrease in adhesion by orders of magnitude would follow from increasing the roughness exponent of a surface (i.e. by making it smoother), and that adhesion could also be lowered by decreasing its lateral correlation length (shorter wavelength). In 2007 [3], we published a simple analytical model, together with experimental data, that demonstrated the strong influence of surface roughness on adhesion. This year, using atomic force microscopy, experimental data were collected from MEMS sidewalls of varying topography but with the same chemical treatment in order to untangle which of the three fractal parameters is – or are – most important in determining adhesion. The data are inconsistent with Chow's predictions; his assumption was that only the asperities on the surface contribute to the adhesion. In contrast, our numerical simulations of the tip-sample adhesion for surfaces with varying fractal parameters include both the asperities and the bulk of the sample.

Together with the simulations, the previous and current experimental data support the conclusion that surface roughness is a significant predictor of adhesion, with the adhesion dropping by more than an order of magnitude for a roughness change from 1 to 10 nm. For the roughness exponent, the simulations follow the same trend as Chow's predictions, in that adhesion should decrease with increasing roughness exponent (smoother), but rather than predicting orders of magnitude change, the simulations reveal only a 20% decrease as the roughness exponent changes from 0 to 1. Here, the experimental data were more consistent with the simulation than Chow's predictions, although they were not conclusive. The scatter in the data was large, and the range of the roughness exponent only varied from 0.85 to 0.99, for which the simulations predict a change in adhesion of approximately 10%. For the lateral correlation length, the experiment showed a wide range of adhesion values for smaller correlation lengths and low adhesion for larger correlation lengths (longer wavelengths); we are still investigating the theoretical basis of this observation. We hope to contribute to the understanding of adhesion so as to minimize stiction in MEMS.

References

1. A.-L. Barabasi and H.E. Stanley, Fractal concepts in surface growth (1995)

2. T.S. Chow, Phys. Rev. Lett. 86, 4592 (2001)

3. D. Liu, J. Martin, and N.A. Burnham, Appl. Phys. Lett. 91 043107 (2007)

10:40am **TR+NS-WeM9 Multiscale Modelling of the Indentation and Scratch Damage of Ultrathin Coatings on Architectural Glass**, ***S.J. Bull***, *A. Oila*, Newcastle University, UK

Although optical coatings are generally designed for their functional requirements it is often the mechanical properties of the system which limits performance. For instance, the major in-service failure mechanism of modern solar control coatings for architectural glass can be scratch damage. Many of these coatings are multilayer structures made from individual layers of less than 100nm thickness and different coating architectures are possible (i.e. different layer materials, thicknesses and stacking order). To assess their mechanical response, coated samples may be subjected to indentation and scratch tests; however, it is not always possible to predict the failure mechanisms of such coatings and modelling approaches have to be developed to understand the deformation mechanisms. This presentation will focus on the problems of measuring the plasticity and fracture properties of very thin coatings (<100nm) and the use of multi-scale modelling approaches to predict performance for coatings on glass.

11:00am **TR+NS-WeM10 Cognitive Molecular Engineering In Nanotribology - Intrinsic Friction Analysis**, *D.B. Knorr*, ***R.M. Overney***, University of Washington

In the new *Age of Molecular Engineering*, one of the objectives is to cognitively design molecules that if condensed, provide materials with anticipated properties. In regards of tribological systems, such as lubricants, the objective would be to offer chemists with molecular design parameters based on which molecules could be synthesized that dissipate energy in a targeted fashion. Thereby, the input would come either directly from experimental observations, or indirectly via computer simulations that are based on models that are relevant to the materials.

This is in contrast to the majority of current research efforts in tribology or nanotribology. State-of-the-art molecular models in tribology focus on generic periodic potentials that are thermally and mechanically inert. Experimental methods provide mostly only phenomenological parameters, such as the friction coefficient, or process descriptive parameters, such as the stick-slip phenomena. Such generic "black-box" approaches, fail to address frictional energy dissipation that are linked to material intrinsic molecular or submolecular modes of relaxation, and hence, do not provide the necessary input for a cognitive molecular design strategy for an effective tribological system.

This talk will highlight the importance of material intrinsic relaxation modes for frictional dissipation involving organic systems. Phenomenological friction analysis data, i.e., friction coefficients from friction-load curves, will be contrasted with spectroscopic data from an intrinsic friction analysis (IFA), involving a time-temperature superposition analysis of friction-velocity isotherms. Both data analysis methodologies, involving lateral force microscopy, reveal an astonishing correspondence regarding the dissipated energy and the energy involved in activating intrinsic relaxation modes and cooperative phenomena. Specifically, we will address surface and sub-surface energy relaxations in amorphous macromolecular model system (e.g., polystyrene) and their relevance to frictional energy dissipation within well defined loading regimes. Depending on the coupling strength (cause for cooperativity) between molecular actuators involved (e.g., rotating side chains or translating polymer backbones) the dissipation in energy can carry a significant entropic energy contribution, accounting for up to 80% of the apparent Arrhenius activation energy. The IFA methodology discussed in this paper that provides direct insight into the enthalpic and entropic energy contributions of friction dissipation processes is shown to be well suited as an analysis tool towards cognitive molecular engineering in tribology.

11:20am **TR+NS-WeM11 Optimization of Tailored Multifunctional Nanocomposite Structures**, ***T. Shenk***, *R. Winter*, *K. Benjamin*, South Dakota School of Mines and Technology

Polymer nanocomposites provide unique solutions to industrial and scientific applications where weight must be minimized and functionality maximized. Researchers are interested in improving the ability to tailor a product to meet specific weight, thermal, optical, mechanical and electrical requirements. Historically functional composite structures have been realized through a top-down approach. With the advent of atomic level measurement tools and experimental techniques a bottom-up approach to the creation of multifunctional structures is receiving intense study. We are developing unique multifunctional structures using such a bottom-up approach with the intent of developing molecular simulations to guide such a process. Properties of polymeric nanocomposite structures are tailored and optimized through a fundamental understanding of intermolecular forces. While macroscopic models of bulk properties of polymer nanocomposites have been characterized, much less is known on the dynamics of their interfacial characteristics, which must be fully developed in order to be able to tailor fabrication of multifunctional nanocomposites using the bottom-up approach. Self assembly, targeted functionalization and spin coating are used to provide consistent means of creating multilayer multifunctional thin film composite strictires allowing for the investigation of multifunctional composites. We investigate the affects of sonication, high shear mixing, and surface modification on the ability to control dispersion to create and predict multifunctional layers of epoxy spin coated nanocomposites and control desired mechanical properties such as conductivity, optical transmission and absorption, loss and storage moduli and coefficient of thermal expansion. The Interfacial Force Microscope (IFM), coupled with the Biaxial Loading Instrument, which allows for refined and uncoupled control of mixed-mode characterization of interface adhesion, will be used to determine interfacial characteristics of these multi-functional composites.

Vacuum Technology
Room: J1 - Session VT-WeM

Partical and Theoretical Aspects of Gas Dynamics
Moderator: R.E. Ellefson, Consultant

8:00am **VT-WeM1 Gas Dynamics Aspects of Atomic Layer Deposition**, ***S.M. George***, University of Colorado at Boulder **INVITED**

Atomic layer deposition (ALD) is a thin film growth method based on sequential, self-limiting surface reactions. ALD can produce extremely conformal and atomic layer controlled film growth. The rate of ALD film growth is dependent on surface reaction efficiencies and gas dynamics. This talk will review the design of various ALD reactors with emphasis on the role of gas dynamics. The optimum pressure in viscous flow ALD reactors will be shown to be a trade-off between gas entrainment and gas interdiffusion. The most rapid rates of ALD film growth will be achieved using "synchronous modulation of flow and draw" where the reactant exposures occur under near static conditions and viscous flow is only operative during reactant purging. The talk will conclude with a review of new ALD reactors operating at atmospheric pressure.

8:40am **VT-WeM3 Collimated Gas Beam Analysis for Atomic Layer Epitaxy of Cracked Disilane**, *M.P. Nadesalingam,* University of Texas at Dallas*, M. Kanouff,* Sandia National Laboratories*, J. Randall,* Zyvex Labs*, R.M. Wallace,* ***W.P. Kirk***, University of Texas at Dallas

The application of collimated gas beams has enjoyed a central role in many atomic and molecular beam experiments of the past, and is again proving to be important for the development of tip based nanofabrication of new devices such as quantum dots, qubits, NEMS oscillators and biomedical devices. We report the analysis of the molecular flux from micro-capillary array dosers for atomic layer epitaxy experiments of cracked disilane. The spatial distribution as well as the total flux can be important parameters for experiments and fabrication processes. Both analytic and numeric analyses have been performed and show values that differ in some aspects from the early results of Winkler and Yates.1 At high acceptance angles where the target is closer to the source, the flux is found to be greater than the previous results by approximately 10 to 15% for various ratios of source to target diameters. The consequences of our results for atomically precise manufacturing of nanometer scale structures will be discussed.2

References

1. A. Winkler and J. T. Yates, Jr., J. Vac. Sci. Technol. **A 6** (5), 2929 (1988).

2. This material is based upon work supported by the Defense Advanced Research Project Agency (DARPA) and Space and Naval Warfare Center, San Diego (SPAWARSYSCEN-SD) under contract N66001-08-C-2040. It is also supported by a grant from the Emerging Technology Fund of the State of Texas to the Atomically Precise Manufacturing Consortium.

9:00am **VT-WeM4 Decomposition Characteristic of Metal-organic Gases**, ***S. Yamashita***, Tohoku University, Japan*, M. Nagase, K. Ikeda,* Fujikin Inc., Japan*, M. Kitano, Y. Shirai, T. Ohmi*, Tohoku University, Japan

The Film formation process by using Metal-Organic (MO) CVD method is used for various applications such as interlayer dielectric of silicon semiconductor devices, ferroelectric substance film formations and transparent electrode formation. MO gases that are used in MOCVD processes are either in the liquid state or the solid state at room temperature and the vapor pressure of these gases is very low. In order to supply MO gases to the process chamber effectively, MO gases are heated to increase the vapor pressure and are supplied by using various means including the bubbling method. But many MO gases have high reactivity. So there is a possibility that MO gases may decompose during use. Due to this problem, there is the issue that byproduct of MO gas decomposition tend to be deposited in the gas supply system. So we evaluated the thermal decomposition property and the oxidation property of three kinds of MO gases [Tetraethoxysilane (TEOS), Trimethylphosphite (TMP) and Trimethylborate (TMB)] by using the FT-IR method to examine the cause of decomposition in MO gases. When MO gases are heated at an inert gas atmosphere, MO gases can be stably supplied without decomposition occurring until 400℃. This result shows that these gases have high stability regarding heat levels. However, when MO gases are heated at an atmosphere including 50 percent oxygen, decomposition temperature of each gas was significantly reduced and carbon dioxide was produced with the decomposition of MO gases. This result shows that the oxidative decomposition of MO gases occurs during heating in an atmosphere including oxygen. Next, MO gases were heated with a resin material used for the valve seat of the gas supply system. We used polyimide (PI) and Perfluoro-Alkoxy (PFA) as a resin material that can be used for the seat of the valve until 150℃. Firstly, TEOS could be stably supplied through tubing containing resin samples. When TMP and TMB flow through the tubing containing the PI test piece, the TMP and TMB could not be stably supplied even at 50℃ and these gases decomposed. And when we raised the heat temperature, decomposition of these gases furthered the progress. When TMP and TMB flow through the tubing containing PFA test piece, the TMB could be supplied stably at 50℃. Afterwards TMP decomposed and could not stably supplied at 50℃. But when TMP continued to flow for a designated duration of time, TMP could be stably supplied. In this case, when we raised the heat temperature, the decomposition of these gases did not occur. This phenomenon was caused by moisture evaporated from resin materials.

9:20am **VT-WeM5 Numerical Simulation of Rarefied Gas Flows through Short Tubes Driven by a Pressure Drop***, F. Sharipov,* Unuversidade Federal do Parana, Brazil*,* ***S. Varoutis****, D. Valougeorgis*, University of Thessaly, Greece

Rarefied gas flows through short tubes are investigated numerically by the Direct Simulation Monte Carlo method. The flow rate and flow field were calculated as a function of the gas rarefaction, length-to-radius ratio and pressure drop. The gas rarefaction, which is inversely proportional to the Knudsen number, is varied from 0 to 2000, i.e. the free-molecular, transitional and hydrodynamic regimes are embraced. A wide range of the length-to-radius ratio, namely from 0 corresponding to the orifice up to 10 representing a sufficiently long tube, are considered. Several values of the pressure ratio between 0 and 0.7 are regarded. This pressure range covers both gas flow into vacuum and into a back ground gas. It has been found that the rarefaction parameter has the most significant effect on the flowfield characteristics, followed by the pressure drop, while the length-to-radius ratio has a rather modest impact. The effect of gas rarefaction on the choked flow and on the Mach discs at large pressure drops is discussed. A comparison of the present numerical results with available experimental data has shown a good agreement.

9:40am **VT-WeM6 Modelling a 25 Stage Turbomolecular Pump with 6 Orders of Compression with DSMC***,* ***R. Versluis****, R. Dorsman*, TNO Science and Industry, The Netherlands

Last year we presented a new method to model moving surfaces in DSMC. The method was validated by modelling a single rotor of a turbomolecular pump and comparison with experimental results. We have now applied the method to model the gas dynamics inside a 25 stage turbomolecular pump (13 rotors and 12 stators) under various discharge pressures and for various gases and gas mixtures. The turbo pump consists of two sections with different number of blades and different angles. The compression of the turbopump is about 6 orders of magnitude and the flow regime insode the pump goes from free molecular conditions at the inlet side to transitional flow on the discharge side. Interesting phenomena inside the pump are shown, such as a non-linear pressure profile inside he pump, with the non-linearity taking place at a position that would not be expected based on the geometry. Details of the gas flow inside the turbopump are visualized such as the concentration profile of gas mixtures inside the pump, temperature effects and the pressure contours inside the pump. All of these things can also be visualized as a function of time showing the pressure increase at the blade edges ahen a rotor passes a stator and the pressure decrease when the rotor has passed the stator, followed by the backflow of molecules in the wake of the blade.

The method allows a completely new look inside the turbopump and offers possibilities for simulation of new prototypes, optimisation of blade geometry, spacing etc. The current algorithm that calculates the interactions between molecules and rotors is limited to linear blade motions. The rotational motion of the blade is therefore linearized to a straight motion, but the method itself is general. The algorithm can easily be replaced for non-linear velocities although the calculation of collisions between blade and molecules becomes more tedious.

By running the calculations a large cluster of dedicated computers (up to 100 parallel nodes) the calculation time for discharge pressures around 1 Pa is still reasonably small (around 1 day).

The attached document shows an example of the results of a calculation for nitrogen.

10:40am **VT-WeM9 New Spiral Molecular Drag Stage Design for High Compression Ratio, Compact Turbo-Drag Pumps**, ***S. Giors***, *L. Campagna, E. Emelli*, Varian S.p.A, Italy

The current turbo-drag pumps commercially available for high vacuum systems are based on either Gaede or Holweck molecular drag stages technology, used in series downstream axial bladed stages to extend the maximum compression ratio up to the 10 mbar foreline pressure range.

Modern Gaede molecular drag stages use a disk shaped impeller, allowing a very compact design, but their maximum compression ratio is limited by the leakage effect to about 10 per stage.

Holweck stages use a less compact drum-shaped impeller, but are able to supply a higher compression ratio per stage and can easily be designed to supply a higher pumping speed thanks to the presence of many channels in parallel.

In this paper a new spiral molecular drag stage design is presented, with the advantages of both high compression ratio and pumping speed per stage and very compact design: a stage occupying the very tiny axial room of a Gaede, can compress as much as two or three Gaede stages in series, and supply the same compression ratio and pumping speed of a Holweck stage of the same diameter and peripheral speed, in a much smaller axial room.

The new spiral drag stage allows the design of very compact, high compression ratio turbo-drag pumps. The comparison of new design turbo-drag pump in the size of 700 l/s with existing Gaede and Holweck based products of the same size is presented, showing the technology advantages of the new design.

11:00am **VT-WeM10 Numerical Analysis of the Rarefied Gas Flow through a Short Channel into a Vacuum**, ***O. Sazhin***, Ural State University, Russia

A rarefied gas flow through a short channel into a vacuum presents a complex task due to significant non-equilibrium. Therefore, it is possible to find a good number of empirical formulas in open literature for calculating flow rate in this case. Correct approach to solving this problem should be based on the Boltzmann equation [1]. The difficulties of numerical solutions for this equation, caused by a large number of independent variables and a complex structure of a non-linear collision integral, are well-known. In our opinion, direct simulation Monte Carlo (DSMC) method [2], which is customarily viewed as a stochastic solution for Boltzmann equation, is preferable for use in tasks with strong non-equilibrium. DSMC method is an effective tool to solve problems of rarefied gas dynamics from free molecular to viscous regimes. An approach based on using DSMC method allows to take into account several factors, such as strong non-equilibrium, as well as to use various models of the gas-surface scattering and the gas molecule-molecule interactions. Therefore, it is appropriate to use DSMC method to study the rarefied gas flow through a short channel into a vacuum.

Practical application of the results of such research can be in the development and creation of such devices as micro- and nanoseparators, micropumps, microshutters, microgyroscopes, micro- and nanosatellites, and other micro- and nanoelectromechanical systems (MEMS/NEMS) [3]. The flow of gas in MEMS/NEMS, depending on device size and gas pressure, can be viscous, transitional or free molecular.

In this study, the mass flow rate through the channel into a vacuum is calculated over the wide range of gas rarefaction as function of channel's length. To study the gas molecule–molecule interaction influence, we used the variable hard sphere and variable soft sphere models defined for inverse–power–law potential and also the generalized hard sphere model defined for the Lennard–Jones potential. Maxwell, Cercignani–Lampis and Epstein models were used to simulate the gas–surface scattering. This study demonstrates that the gas molecule–molecule interaction and the gas–surface scattering can have a significant influence on the rarefied gas flow through a short channel into a vacuum. The analysis of the flow field, both within the channel as well as in upstream and downstream containers, is presented.

REFERENCES

1. C. Cercignani, *The Boltzmann Equation and its Application*, Springer, New York (1988).

2. G.A. Bird, Molecular Gas Dynamics and the Direct Simulation of Gas Flow, Oxford University Press, Oxford (1994).

3. *Encyclopedia of Microfluidics and Nanofluidics*, ed. by Dongqing Li, Springer, New York (2008).

11:20am **VT-WeM11 Effect of Surface Material and Roughness on Conductance of Channel between Parallel Disks at Molecular Flow**, ***H. Yoshida***, *M. Shiro, K. Arai, M. Hirata, H. Akimichi*, National Metrology Institute of Japan / AIST, Japan

For precise calculations of conductance and pressure distribution in vacuum chamber at molecular flow, it is important to know a degree of realization of diffuse reflection (also called cosine law) at surface. The conductance of an experimental channel changing the surface material and roughness was measured and compared with the results using Monte Carlo calculation assuming diffuse reflection.

The experimental channel consisted of two parallel disks was equipped with the vacuum chamber with an inner volume of 8.42x10-2 m3.The lower disk made from polished stainless steel (SS) has a diameter of 40 mm and a hole of 10 mm in diamter at the center. The upper disk with 51 mm in diameter is located as facing parallel to the lower one. The space between the upper and the lower disks was determined from 0.3 mm to 0.7 mm using gauge blocks as a spacer. After the vacuum chamber was filled with N2, Ar, or He gas at approximately 100 Pa, it was evacuated from the hole of lower disk by turbo molecular pump (0.22 m3/s) through the space between two parallel disks. The conductance of the channel was obtained from the pressure decrease rate in the vacuum chamber.

Eleven upper disks with different material and surface were prepared: polished SS, unpolished SS, quartz, Ti, Cu, Al, alumina with smooth surface, alumina with rough surface, SS with Au coating, SS with Pt coating, and SS with DLC coating. The effect of surface material and roughness on conductance was estimated from the measurement of the conductance of the channel by replacing the upper disk.

The conductance for N2 using polished SS with 0.5 mm in space was 3.68x10-4 m3/s (±2.7%), which was comparable to the calculated value of 3.67x10-4 m3/s (±1.3%). Similarly, the experimental values for N2 and Ar using polished SS, quartz and SS with DLC coating showed good agreement with the calculated ones within the measurement uncertainty. On the other hand, the conductance using SS with Pt coating was about 7% smaller than the calculated one. Their surfaces morphologies were analyzed by optical microscope and atomic force microscope (AFM). The microscopic surfaces of polished SS, quartz and SS with DLC coating were very smooth with the roughness less than 1 nm and the specific area less than 1.01. In the case of SS with Pt coating, however, the microscopic surface was rough with the specific area of 1.10. Judging from the results of all disks, the conductance seemed to be influenced by surface roughness rather than surface material. In the case of He, the experimental value was about 4% larger than the calculated one. This reason should be the influence of the specular reflection and/or the lobular scattering.

Exhibitor Workshops
Room: Exhibit Hall 1 - Session EW-WeL

Exhibitor Workshop
Moderator: R.A. Langley, Consultant

12:40pm **EW-WeL3 Time and Phase Resolved Plasma Diagnostics for RF and Pulsed Plasma Applications**, ***M. Hopkins***, Impedans Ltd.

The deposition and etching of layers by plasma discharges operating in pulsed mode have many important applications. The variation of the time parameters of the process (frequency and duty cycle) lead to noticeable modifications of the deposited layers and the etch rate. Plasma diagnostic are now available to measure the change in plasma composition and this is turn is often correlated with the quality of the process. In diamond thin films the quality of films produced is strongly correlated with the concentration of H-atoms, CH and C2 radicals and their evolution during the discharge regime and the afterglow. Indeed, these species are well known either as agents for graphite etching (H), or diamond precursors (CHx imaged by CH) or graphite precursors (C2Hx imaged by C2). In silicon etching anomalous side wall etching, called 'notching' in gate poly-Si etching, is suppressed in pulsed-power chlorine inductively coupled plasma. In order to understand the complex mechanisms involved in pulsed or indeed RF plasma a comprehensive suite of time and phase resolved measurements have been developed by Impedans. In this presentation we will show dependent measurements of ion energy distribution, plasma potential, electron and ion density/flux and electron temperature data in pulsed and RF plasma illustrating the complex changes occurring when time modulation is used in plasma processes.

1:00pm **EW-WeL4 Modern e-Gun Evaporation Simplified for Research and Pilot Production Applications**, ***J. Moore***, *M. Ricks*, Thermionics Vacuum Products

Over the past 50 years electron beam sources have gone through numerous transformations. As the vacuum coating industry has evolved, electron guns have advanced from simple permanent magnet sources to sources with advanced magnetics and electromagnetic sweeping to meet the numerous application needs.

In the late 1980's, Thermionics' HM2 sources introduced discrete modular magnet technology which allowed beam shapes to be optimally configured for a process. This also provided a mechanism for advancing co-deposition making possible a source that could evaporate 6 materials simultaneously with complete independent control while maintaining extremely close crucible locations. The introduction of high frequency beam sweep helped to further increase the uniformity of the e-beam temperature making the sources more reliable

Modern sources such as the Thermionics' RC and HC e-Guns utilize traditional magnets with a series of modified pole extensions to create the effect of a discrete modular magnet source while still providing a "simple to service" source. Other features such as dual filament emitter assemblies and plug in emitter modules allow a high level of performance with minimum maintenance and technical expertise. This new generation of sources blend the past function oriented source with the modern high performance source allowing the average graduate student or research scientist access to the full spectrum of e-gun evaporation.

While sources have evolved, system technology has also been steadily moving forward. New systems incorporate hinged quick access doors and fully automated computer controls. Thermionics latest machine tools go one step further with cartridge loaded sources and sample holders. This new level of flexibility allows a research group to change process recipes in just minutes.

1:20pm **EW-WeL5 Modeling Electron Impact Collisions of Gas Mixtures Using Particle-in-Cell (PIC) Code**, ***S. Mahalingam***, *S. Veitzer*, *P.H. Stoltz*, Tech-X Corporation

We are developing a Monte Carlo Collision (MCC) model in VORPAL, a three-dimensional particle-in-Cell (PIC) plasma simulation code that will self-consistently model various types of electron impact collisions with a neutral gas (or) a combination of gas mixtures. The MCC model will include elastic (such as elastic scattering, and large-angle elastic scattering), inelastic (such as excitation, and ionization) and Bremsstrahlung collisions. A null collision technique is used for handling the electron impact collisions. The collision cross sections data are based on the Evaluated Electron Data Library (EEDL) dataset, which we obtained from the International Atomic Energy Agency Nuclear Data Services (IAEA NDS). The EEDL library contains collision cross sections and generation data for electrons and photons for atoms with Z = 1 – 100 for incident electron energies from 10 eV (or threshold) to 100 GeV. Additionally, we will enable the elastic scattering cross section data available for low incident electron energies (below 10 eV) from known measurements, so that the MCC model can be applied for studying the low temperature plasma problems. Users also have the option of specifying a user-defined model of the cross section. We will show simulation results for gases and parameters relevant to the plasma processes involved in the breakdown of metallic structures occurring in high-gradient RF cavity experiments.

*The work of Tech-X personnel is funded by the U. S. Department of Energy under Small Business Innovation Research (SBIR) Contract No. DE-FG02-07ER84833.

1:40pm **EW-WeL6 Near Ambient Pressure XPS - In Situ Surface Analysis Under Extreme Conditions**, ***A. Thissen***, SPECS GmbH, Germany

Applied Surface Science
Room: C2 - Session AS-WeA

Angle-resolved X-ray Photoelectron Spectroscopy
Moderator: A. Herrera-Gómez, CINVESTAV-Qro, Mexico

2:00pm **AS-WeA1 ARXPS: Power and Limitations in the Search for New Microelectronics Materials and Processes**, ***T. Conard***, IMEC, Belgium **INVITED**

While the concept of Angle-resolved XPS has been available since the early days of XPS, its use has always been limited both due to its demanding experimental overhead and the difficulties of data interpretation. The introduction of systems allowing recording several angles in parallel has greatly eliminated the experimental difficulties and pushed the development of more integrated software's for data interpretation. Simultaneously, the advent of use of very thin film across many industries and especially for high-k dielectric in the microelectronics industry, the ability to accurately and quickly evaluate the true composition, including species location within a layer, has become more complicated, or even impossible. Specifically, a depth profile involving ion sputtering will cause a rearrangement of species by degrading the analytical results. Non sputtering techniques such as ERD or MEIS have achieved high quality, quantitative depth profile on very thin layers. However, ERD and MEIS are complex techniques from both an instrumental and theoretical point of view. This paper will present the possibilities of composition depth profiling for thin films (<5nm) by XPS without the need for sputtering. We will however emphasize the danger of blindly applying the technique through the use of several examples. The use of ARXPS is however not limited to depth profiling of ultra-thin layers. We will also include example of application in the field of organic chemistry, bio-sensors, etching and cleaning process development, where the additional qualitative information available through angle-resolved measurement significantly simplify the interpretation of the data.

2:40pm **AS-WeA3 Effects of Elastic Scattering and Analyzer-Acceptance Angle on the Analysis of Angle-Resolved XPS Data**, ***C.J. Powell***, National Institute of Standards and Technology, *W.S.M. Werner, W. Smekal*, Vienna University of Technology, Austria

Angle-resolved XPS is frequently used to obtain composition-depth information. Reliable analysis of the data, however, is currently based on the validity of a number of assumptions that include neglect of elastic scattering and neglect of the analyzer-acceptance angle. We determined XPS intensities of N 1s, O 1s, Hf 4f, Si (oxide) 2p, and Si (substrate) 2p peaks at selected emission angles for $SiO_{1.6}N_{0.4}$ and $HfO_{1.9}N_{0.1}$ films on Si with thicknesses of 5 Å, 15 Å, 25 Å, 35 Å, and 45 Å. The intensities were calculated using the NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA) [1,2]. Simulations were performed for Al Kα X-rays, sample tilting, and differential elastic-scattering cross sections from the relativistic partial-wave expansion method (Mott cross sections). We also performed simulations with the straight-line approximation (SLA) in which elastic scattering is neglected. We will report comparisons of peak intensities for four models: (a) Mott cross sections and an analyzer semi-angle of 12^o, (b) Mott cross sections and a semi-angle of 0.5^o, (c) the SLA and a semi-angle of 12^o, and (d) the SLA and a semi-angle of 0.5^o. The intensity ratios changed appreciably as elastic scattering is switched on and off, but changing the analyzer semi-angle had a smaller effect. These changes are comparable to those found in N 1s and O 1s angular distributions for different N composition profiles in SiON, thus casting doubt on the validity of N composition profiles obtained from conventional analyses of ARXPS data. We will present plots of ratios of intensities for each line obtained from Models (d) and (a) as a function of emission angle for each film thickness. The largest change occurred for the substrate Si 2p line where the ratio increased appreciably with emission angle, reached a maximum in the vicinity of 50^o to 60^o, and then decreased rapidly. These changes were more pronounced in the HfON films than the SiON films, indicating the stronger elastic-scattering effects in HfON than in SiON. We will report similar comparisons with Cu Kα X-rays. Although elastic-scattering effects are less pronounced than at lower energies, they are not negligible. A planned enhancement of SESSA to include polarized X-rays will make it useful for XPS applications with synchrotron radiation. [1] http://www.nist.gov/srd/nist100.htm.

[2] W. Smekal, W. S. M. Werner, and C. J. Powell, Surf. Interface Anal. **37**, 1059 (2005).

3:00pm **AS-WeA4 Combining Angle-Resolved and Inelastic Background Information into Concentration-Depth Profiles; A Massively-Parallel Algorithm and a New MEMS Electron Analyzer**, ***P. Cumpson***, Newcastle University, UK

We present new, fast algorithms for automated depth-profiling by Angle-Resolved XPS and AES, and first results from a microfabricated electron energy analyzer array optimised for use with them.

The period to 1995 saw the development of good models for simulating XPS spectra, often based on Monte Carlo simulation[1]. These helped in improving understanding, but were too slow to help analysts interpret particular spectra directly. Also these calculations were in the opposite direction to that desired - spectra were calculated from composition, whereas what we need is the reverse. Nevertheless, progress was made in speeding these calculations substantially[2].

In addition to the usual improvement in CPU speed since then, more of a surprise perhaps is the emergence of PC Graphics Processing Units ("GPUs"). No longer simple arrays of screen memory, these contain tens - often hundreds - of separate processors on one chip. Typically they are used for ray-tracing, following single rays of light back from the detector (a human eye) to their origin, including various types of scattering, reflection and refraction. They do so in parallel, and are used intensively in computer games. We can capitalise on the similarity to electron transport. We have developed algorithms to use these GPUs to simulate XPS and AES emission processes - and in the direction we need - that is, from measured spectrum back to determine the original concentration depth-profile. Most medium-power PCs typically have a suitable graphics card already installed. We have demonstrated a speed-up of roughly 20 times on a 240 processor GPU card, compared to the PC CPU alone, making the time taken for calculation of the composition-depth profile similar to the that of acquiring the spectra in many cases - so it can potentially be done in "real time".

The flexibility of these algorithms mean that the chemical information in spectra can be extracted even if analyzer performance (transmission, resolution, scattering) is poorer than that of modern analyzers, but one needs at least three emission angles[3]. Therefore we have fabricated an array of three silicon MEMS analyzers, similar to a type previously proposed for plasma measurements from spacecraft. We present initial results, though there are significant issues of low transmission and scattering compared to macroscopic hemispherical sector analyzers. We expect to improve their performance to the point where they can be used in conjunction with our GPU algorithms.

[1] A Jablonski and J Zemek, Phys Rev B 48, 4799-4805 (1993)

[2] P J Cumpson, Surf. and Interface Anal. 20, 727 (1993)

[3] P J Cumpson, J. of Elec. Spectrosc., 73 25 (1995)

4:00pm **AS-WeA7 Application and Optimization of Depth Profile Reconstruction from XPS Data using the Maximum Entropy Method**, ***G.J. Mishra***, Kratos Analytical Ltd, UK, *D.J. Surman*, Kratos Analytical, *K.C. Macak*, Kratos Analytical Ltd, UK

Angle resolved X-ray Photoelectron Spectroscopy (ARXPS) is a useful method for obtaining nondestructive quantitative information about the depth distribution of chemical components in thin (2– 8 nm) films. Modern instrumentation makes the collection of large amounts of data straight forward but determining the depth distribution of elements is more challenging. One numerical method commonly applied to this type of data is the maximum entropy method (MEM). For the MEM to be successfully applied and a depth profile reconstructed, the experimental data must be consistent with the physical model describing the electron transport in the sample. The precision of the reconstructed depth profile depends both on the noise in the experimental data and on the accuracy of the physical model. The Beer-Lambert law of electron transport which is used for routine analysis of the experimental data provides inadequate description of the elastic scattering effects and doesn't account for the finite analyser acceptance angle.

We present a more refined model of the MEM algorithm based on a depth distribution function which allows the consistent inclusion of the aforementioned effects of scattering and analyser acceptance angle into the analysis of depth profiles. Direct incorporation of the depth distribution algorithm into the MEM model also allows the utilization of the results of Monte Carlo simulations of electron transport instead of various approximate attenuation length parameters.

The effect of data collection conditions, in terms of instrument operating mode; analyser collection angles; and signal to noise, on the reliability of reconstructed profiles is also investigated. A set of optimised conditions and minimum data quality for successful depth profiling of the materials under investigation are suggested.

4:20pm **AS-WeA8 A Case Study of Depth Profile Reconstruction from Parallel ARXPS Data by Application of a Genetic Algorithm : Characterization of a Novel, Low-Energy Plasma Treatment***, P. Mack,* ***R.G. White****, J. Wolstenholme,* Thermo Fisher Scientific, UK*, E.H. Lock, S.G. Walton,* Naval Research Laboratory*, D.Y. Petrovykh*, Naval Research Laboratory and University of Maryland, College Park

Maximum entropy methods are often used to reconstruct depth profiles from angle resolved XPS data. Such methods typically rely on searching a vast parameter space for potential solutions, but in the past, it has been left to the analyst to decide when the optimum solution has been identified. An undesirable side-effect of this approach is that different analysts are likely to reconstruct different depth profiles from the same ARXPS data set. By contrast, depth profile reconstruction software based on a genetic algorithm rapidly samples many thousand potential solutions in the maximum entropy parameter space, but only reports the optimum result without input from the analyst,

This approach has been applied to characterize the surfaces generated by a new, low-energy plasma treatment. Polystyrene films, modified by a variety of plasmas, were analysed using parallel angle resolved XPS (PARXPS). An evaluation of different methods of ARXPS depth profile reconstruction was performed, comparing “boxcar” and “Cumpson” models with maximum entropy method results. The maximum entropy calculations employed the genetic algorithm to search for the optimum solutions. The non-destructively measured PARXPS profiles were compared with low-energy argon sputter profiles of the polymer surfaces.

Additionally, angle resolved reflection electron energy loss spectroscopy (AREELS) measurements were performed, giving depth-dependent information on the level of carbon unsaturation in the plasma-modified regions of the surface.

This work was supported by the Office of Naval Research.

E. H. Lock is NRL/NRC Postdoctoral Research Associate.

4:40pm **AS-WeA9 Advantages of AR-Hard X-ray Photoelectron Spectroscopy (HAXPES) in the Characterization of Advanced Semiconductor films.***, **G. Conti**, Y. Uritsky,* Applied Materials Inc.*, C. Papp, C.S. Fadley*, Lawrence Berkely National Laboratory

High-dielectric constant materials such as HfO2 and metal gates such as TiN are promising materials for the fabrication of high speed, low power consumption devices.

In these systems, the control of the interfaces between the dielectric materials and the electrodes is crucial. Effects such as intermixing, chemical reactions, formation of crystalline domains, etc. require detailed investigation, especially in the new metal gate materials replacing the poly-silicon electrode. Angle –resolved soft X-ray XPS is often employed to probe chemical and structural changes of the individual dielectric and metal layer. Material intermixing, oxygen vacancies and molecular structure at the interfaces play a fundamental role in predicting the electrical performance of the final devices. Probing the entire film stack without any manipulation (spattering, FIB, etc.) is a big challenge for all the metrology presently available in the industrial analytical laboratories. Collaborations between industry and universities may greatly help in developing these advanced devices.

In this work we present the “non destructive” characterization of the total film stack by Hard X-ray AR-XPS (X-ray energy~ 6000eV). This film, under development for 32nm node technology, consists of 50A poly-Si and 100A TiN as a metal gate, of 20A HfO2 as a high dielectric constant material, of a 10A SiO2 on Si substrate.

. This paper will report recent results on chemical and structural information obtained at the TiN/HfO2 interface. Intermixing of TiN and HfO have been observed by TEM analysis, but for the first time we can show that the Hf4f is sensitive to its environments and shows a multiple peak structure probably due to Hf bonded to O and to N.

5:00pm **AS-WeA10 Evaluation of ARXPS for Thickness and Composition Determination for Typical Wafer Processing Thin Films***,* ***C. Brundle****,* C. R. Brundle and Associates*, G. Conti*, Applied Materials

ARXPS can be used in two ways to obtain depth distribution information for the near surface region of materials. The first is the Relative Depth Profiling (RDP) approach, which is completely qualitative and provides a "layer ordering" under certain conditions (the material has to be genuinely approximatable by a layer structure and a given XPS resolvable species should not be present in more than one layer). Provided there is sufficient signal intensity to be observed at two angles, the method is usable, which often means qualitative information beyond 100Å depth can be obtained. The second approach is to model the data based on inelastic mean free path lengths, the Beer-Lambert law, and some degree of entropy contribution (such as the Max Entropy approach), in an attempt to produce a quantitative profile. With no constraints there are a huge number of fittable parameters (every species concentration at every depth) and reliable results cannot be obtained. Introducing reasonable constraints (as may be expected, or already known, for wafer processing thin film structures), such as sharp interfaces, known layer ordering, and fixed compound stoichiometry, can reduce the number of parameters to the point where the required accuracy of the experimental data (separation of signal intensity from background; exclusion of data where elastic scattering becomes an issue) necessary to give reliable fits can be achieved. However, owing to the exponentially decreasing contribution to the total signal strength with depth, this cannot be extended beyond about 2λ in depth (which means 40 -50Å) and, in addition, the true depth resolution possible is poor.

Examples of the successful use, and the misuse, of the ARXPS approach for the types of ultra-thin film structures found in wafer processing (involving Si, SiO2, Si3N4, SiOxNy, Hf oxide based layers, and TaN) will be presented. In practical situations, where the intended recipient of the end results is not an an XPS "afficionado", communication of the data in a form that does not lead to gross over-interpretation remains an issue.

5:20pm **AS-WeA11 Development of ARHXPS System using Wide Acceptance Objective Lens and Compact Monochromatic Cr Kα X-ray Source***,* ***K. Kobayashi****, M. Kobata,* NIMS Beamline Station at SPring-8, Japan*, H. Iwai,* NIMS, Japan*, H. Yamazui, H Takahashi, M. Kodama, M. Suzuki,* ULVAC PHI Inc., Japan*, E. Ikenaga, M. Machida, J.Y. Son,* SPring-8/JASRI, Japan*, H. Mastsuda, H. Daimon,* NAIST, Japan*, H. Nohira*, Tokyo City Univ., Japan

In the course of the development of hard X-ray photoemission spectroscopy (HXPS) using high flux high brilliant undulator X-rays[Nuclear Instruments and Methods in Physics Research A 601 (2009) 32–47], we were convinced that HXPS is a powerful versatile tool for the research in the basic and applied science and technology. This lead us to development of a laboratory ARHXPS system by combining a focused monochromatic CrKα X-ray source, a wide angle acceptance objective lens, and a high kinetic energy electron analyzer. The CrKα source consists of Cr target, 20 keV focused electron gun, and compact bent crystal monochromator. The X-ray spot is variable from 10 μm (1.25 W) to 200 μm (50 W). The wide acceptance objective lens using an ellipsoidal metal mesh electrode is designed by H. Matsuda and H. Daimon [Phys. Rev. E 71 (2005) 066503] . This objective lens is installed in front of a VG SCIENTA R4000 10kV hemispherical analyzer. The total resolution of 0.5 eV was verified by Au Fermi edge measurements. Angle acceptance of ±35 deg with angle resolution of 0.5 deg was confirmed by measuring Au 3d$_{5/2}$ peak of Au thin strip covered with a hemi-cylindrical multi slit, in angle resolution mode. Seven times enhancement of the throughput was affirmed by comparing intensities of Au spin-orbit doublet peaks with and without the objective lens. The Si1s, Hf3d, and valence band spectra of a HfO_2(4 nm)/SiO_2 (1 nm)/Si (001) sample were measured to test the practical applicability. Acquisition times of 5 min, 10 min, and 12 hr were found enough to obtain spectra with good S/N ratio. In order to evaluate effect of overlayer on the photoelectron diffraction (XPD), polar-azimuth angle 2D mapping of Si1s intensity of Si(001) substrates was carried out in samples covered with thin natural oxide, 4 nm SiO_2, and 7 nm SiO_2. It was verified that XPD intensity modulation was clearly observed even in the 7 nm SiO_2 overlayer substrate. Another trial was to detect chemical change in buried interface of an Ir (10 nm)/HfO_2 (2.2 nm)/wedge shape SiO_2 (0-10 nm) /Si (100) sample. The Si1s (both substrate and oxides) and O1s spectral shapes were found to change along the thickness variation of the wedge.

In conclusion, the CrKα laboratory ARHXPS system was verified to be a promising tool for the investigation of bulk and thin solid film materials. The potential applicability of the system to the depth profiling of layered materials of more than 10 nm thickness is to be realized. Strong XPD modulation of the crystalline substrate may causes a certain difficulty to the depth profile analysis

We are thankful to Dr. Miyata and Dr. Abe of AIST for providing us Ir/HfO_2/SiO_2/Si(001) sample.

This work was supported by SENTAN, JST.

Biomaterial Interfaces
Room: K - Session BI+AS+NS-WeA

Quantitative Nanoscale Sensing at Biosurfaces and Interfaces
Moderator: F. Höök, Chalmers University of Technology, P. Kingshott, Aarhus University, Denmark

2:00pm **BI+AS+NS-WeA1 Characterizing Self-Assembled Supported Lipid Membranes for Biosensing**, ***E.O. Reimhult***, ETH Zurich, Switzerland **INVITED**

More than 50% of all drug targets are membrane proteins, which require a lipid membrane environment to retain correct conformation and function. This highlights the need to create sensing tools for analytical profiling of transmembrane protein function subject to e.g. drug binding. Furthermore, it is increasingly realized that the compositionally complex and dynamically rearranging lipid membranes can be important active regulators of biological function in their own right. The complexity of the *in vivo* cell membrane and the need to apply high throughput techniques like arrays and highly surface sensitive analytical techniques make model systems highly desirable. Thus, supported lipid bilayers (SLBs) which combine control of membrane properties with surface analytical techniques receive increasing interest.

Biosensor interfaces can be easily functionalized with an SLB by self-assembly from liposomes. However, design of more native-like SLBs, e.g., having diverse lipid compositions, including glycolipids or mimics thereof, demands further developments of this assembly technique. This in turn prompts for more advanced characterization of the formation and structure of SLBs.

We present advances in instrumentation and interpretation of data from multi-technique studies of liposome adsorption and SLB formation, which enhance the understanding of the assembly process and the sensor response obtained for different membrane conformations. In particular, we demonstrate advances in waveguide spectroscopy which allow for characterization of the rupture kinetics of supported lipid bilayers by liposome fusion, but also to in real time distinguish differences in structure for membranes of different compositions and under various environmental conditions. These advances also open the possibility to study differential binding to and into SLBs and to use rearrangements in the SLB as an amplifier of membrane protein binding events.

As examples, we also present the results of such detailed multi-technique characterization of the self-assembly of new supported lipid membrane mimics, e.g., bacterial membrane mimics containing lipopolysaccharides and poly(ethylene glycol)-lipids, including how the presence of a polymer directly attached to the lipids affects the self-assembly and how the hydrophilic polymer is distributed and rearranged in the membrane under mechanical perturbation. Such self-assembled polymer-membranes have great potential for creation of membrane arrays incorporating membrane proteins thanks to high stability and less perturbation of the membrane components due to the mobile polymer spacer layer.

2:40pm **BI+AS+NS-WeA3 Nanoplasmonic Biosensing: Artificial Cell Membranes, Structural Changes and Quantification of Bound Mass**, ***M. Jonsson***, *A. Dahlin, P. Jönsson, S. Petronis, F. Höök*, Chalmers University of Technology, Sweden

The resonance condition for excitation of plasmons associated with metal nanostructures is highly sensitive to changes in the interfacial refractive index, which has made the phenomenon highly popular as transducer principle for label-free sensing of biomolecular recognition reactions. There is a particular need for sensor concepts that are compatible with studies of the cell membrane, which can be explained from the fact that more than half of the most commonly used drugs are directed towards membrane-associated reactions. This is also relevant with respect to diagnostics of viral diseases, because viruses typically infect host cells via adsorption to the cell membrane. During the past years we have developed nanoplasmonic biosensing platforms that are compatible with studies of artificial cell membranes, such as lipid vesicles and supported lipid bilayers (SLBs).[1-3] In addition to probing specific binding of ligands to membrane receptors, we showed that nanoplasmonic sensors provide a unique means to probe biomolecular structural changes, such as during the formation of a SLB from adsorption and rupture of lipid vesicles.[1]

We have previously used a metal film perforated with nanoholes as an electrode for combined nanoplasmonic and quartz crystal microbalance measurements.[3,4] Besides two independent measures on biomolecular structural changes, the combined sensor setup was shown to provide new information that enabled the quantification of adsorbed mass on the sensor surface with only the density of the molecules as unknown parameter.[3]

In the current work we utilize the continuity of a perforated plasmon active metal film to fabricate nanoplasmonic pores with liquid access to both sides of the nanopores.[5] This structure opens up for a wide range of novel applications. For example, extending our previous work on plasmonics and cell membrane mimics, an appealing possibility is to measure transport of both charged and non-charged molecules through lipid membranes that span the pores. Plasmonic pores can also be used for flow-through sensing, where flowing the target molecules through the pores will facilitate molecules to reach the sensor surface in an efficient way and circumvent limitations due to mass-transport.[6]

References:

1 Jonsson, M. P. et al. *Nano Letters* **2007**, *7*, 3462-3468.

2 Dahlin, A. B.; Jonsson, M. P.; Höök, F. *Advanced Materials* **2008**, *20*, 1436-1442.

3 Jonsson, M. P.; Jönsson, P.; Höök, F. *Analytical Chemistry* **2008**, *80*, 7988-7995.

4 Dahlin, A. B.; et al. *ACS Nano* **2008**, *2*, 2174-2182.

5 Jonsson M. P. et al. Manuscript in preparation

6 Eftekhari F. et al. *Analytical Chemistry* **2009**, ASAP

3:00pm **BI+AS+NS-WeA4 Transfer of Biomolecules between Lipid Membranes**, ***A. Kunze***, *S. Svedhem*, Chalmers University of Technology, Sweden, *P. Sjövall*, SP Technical Research Institute of Sweden, *B.H. Kasemo*, Chalmers University of Technology, Sweden

The study of the interaction between biomembranes is of great interest for both basic research and applications in biosensing technology. In biological systems the interaction between membranes including transfer of biomolecules plays a pivotal role. For instance, it is central in energy supply to and communication between cells and for the function of a large number of drugs. A controlled transfer of lipid molecules, or other biomolecules, between lipid vesicles (liposomes) and solid supported lipid bilayers (SLBs) provides a new platform for modifying and controlling SLBs that can be used in biosensing technology. Mechanistic studies of this process are furthermore important for the understanding of a number of important biomolecule-membrane and inter-membrane events.

We will present how transfer of biomolecules between an SLB and liposomes can be monitored in real-time giving more insight into the complex mechanism of transfer including influence of electrostatic interaction, ionic strength, phase and molecular structure of lipids, as well as time scale of the transfer process. Recent results show that the interaction process consists of an attachment-transfer-detachment (ATD) sequence, where added liposomes first attach to a preformed SLB, then transfer lipid molecules and eventually detach, leaving behind a compositionally modified SLB and ditto vesicles.[1] We will demonstrate how the ATD process can be used for *in situ* modifications, changing the membrane composition, e.g. for the formation of a highly stabilized (SDS-resistant) lipid monolayer on TiO_2, which can then be used for the reassembly of an SLB.[2] We propose this as a promising method for *in situ* preparation of asymmetric SLBs.

The main experimental techniques used to study these processes at these interfaces between two biomembranes are the quartz crystal microbalance with dissipation monitoring (QCM-D), t otal internal reflection fluorescence microscopy (TIRF), fluorescence microscopy and time-of-flight secondary ion mass spectrometry (TOF-SIMS) and optical reflectometry.

[1] Kunze, A.; Svedhem, S.; Kasemo, B. Lipid Transfer between Charged Supported Lipid Bilayers and Oppositely charged Vesicles, Langmuir in press

[2] Kunze, A.; Sjövall, P., Kasemo, B.; Svedhem, S. In situ preparation and modification of supported lipid layers by lipid transfer from vesicles studied by QCM-D and TOF-SIMS, J. Am. Chem. Soc., 131:2450-2451, 2009

4:00pm **BI+AS+NS-WeA7 Nanopores for Sensing Membrane Processes and Enzyme Reactions**, ***M. Mayer***, University of Michigan **INVITED**

This talk demonstrates that pores with diameters below 50 nanometers make it possible to detect enzyme reactions, molecular phases transitions, and nanoscale self-assemblies *in situ* and in real time. For instance, coating the inner walls of nanopores with self-assembled lipid bilayers, afforded controlled shrinkage of this pore to a size that made it possible to detect individual proteins. Remarkably, the extent of pore shrinkage could be controlled with sub-nanometer precision by the chain lengths of the acyl chains on the lipids that were chosen to assemble the bilayer. Due to the extreme sensitivity of single-channel recording of ion currents through nanopores, this approach made it possible to monitor molecular changes and rearrangements of the lipid bilayer. These changes included phase transitions, variations in membrane composition, and enzymatic reactions on membranes. For example, this approach made it possible to monitor the activity of attomolar amounts of phospholipase D (PLD) and phospholipase C (PLC) – two membrane-active enzymes that are critical for cell signaling.

4:40pm **BI+AS+NS-WeA9 Development of Microresonator Arrrays for Mass and Viscoelastic Characterization of Adsorbed Molecular and Biomolecular Thin Films**, ***D.L. Allara***, *S. Tadidagapa, P. Kao*, Pennsylvania State University

A multiple pixel micromachined quartz crystal resonator array with a fundamental resonance frequency in the 60-100 MHz range has been designed, fabricated, and tested for applications to accurate mass and viscoelastic measurements of adsorbed thin molecular and biomolecular films. Operating with high Q-factors in the range of 25000–50000 and appropriately lower in liquids, the high stability and inherent low noise of the quartz crystals allow for an unprecedented resolution of one part in 10 million for density/viscosity variations. Further, multiple pixels, capable of independent functionalization with SAMs, can be tracked in parallel to give large numbers of independent measurements simultaneously. By measuring the frequency decrease at overtone frequencies it also is possible to vary the decay length of the shear wave away from the electrode and thereby identify individual variations in the density and viscosity of the local environment and accurately monitor small changes in the viscoelastic loading of adsorbed films. The performance of the resonator is illustrated with examples such as the adsorbed protein films in which the damping factor undergoes an order of magnitude change in transitioning from monolayer to multilayer adsorption. This aspect is highly desirable for accurate determination of behavior such as conformational changes.

5:00pm **BI+AS+NS-WeA10 Plasmonically Coupled Nanoparticle-Film Molecular Ruler**, ***R.T. Hill***, *J.J. Mock, A. Degiron, S. Zauscher, D.R. Smith, A. Chilkoti*, Duke University

Experimental analysis of the plasmonic scattering properties of gold nanoparticles controllably placed nanometers away from a gold metal film shows that the spectral response of this system results from the interplay between the localized plasmon resonance of the nanoparticle and the surface plasmon polaritons of the gold film, as previously predicted by theoretical studies. In addition, the metal film induces a polarization to the single nanoparticle light scattering resulting in a doughnut-shaped point spread function when imaged in the far-field. Both the spectral response and the polarization effects are highly sensitive to the nanoparticle-film separation distance, and thus, the plasmonically coupled NP-Film system represents a new variant of the previously reported plasmonic molecular rulers. A surface-based molecular ruler shows promise in potential biosensor and diagnostic devices.

5:20pm **BI+AS+NS-WeA11 Label-free Imaging of Cell Adhesion Dynamics using Surface Plasmon Resonance Imaging Ellipsometry**, ***D.W. Moon***, *J. Gil, W. CheGal, H. Cho, S. Kim*, Korea Research Institute of Standards and Science, S. Korea

The interaction between cell and extracellular matrix (ECM) governs multiple cellular functions and contributes to promote inflammation and tumor metastasis. Therefore, cellular behavior needs to be monitored in the ECM interactive circumstance. Most of previous studies on cell adhesion are based on immunofluorescence microscopy. For cell adhesion dynamics studies, label-free optical techniques that can monitor continuously cell-ECM interfaces for living cells are required.

Here we developed surface plasmon resonance imaging ellipsometry (SPRIE) which can simply image cell-ECM interfaces for live cells with high contrast and at real-time. To visualize cell adhesions to ECM, null-type imaging ellipsometry technique with the attenuated total reflection coupler was applied and both of transverse magnetic and electric waves were made use of. These characteristics make it possible to acquire the high contrast image of cell adhesions. Different features and dynamics of cell adhesion patters in ~ 100 nm cell-ECM interfaces were observed for A10, human coronary artery smooth muscle cell hCASMC, and human umbilical vein endothelial cells (HUVEC) on fibronectin and collagen ECM layers with 1 µm spatial resolution and 30 sec time interval upto 3 days. Harmonized changes of entire adhesion proteins were observed during cell division and cell migration through our imaging system without any labeling. SPRIE images were compared with confocal fluorescence microscopic images of cell adhesion proteins for validation of SPRIE images. Preliminary results on SPRIE studies on the effect of shear force on cell adhesion and migration will be also discussed.

We expect that SPRIE cell adhesion dynamic imaging methods would be useful for further understanding of cell biology and development of drug screening methodology relevant to cell adhesion and migration.

5:40pm **BI+AS+NS-WeA12 Label-Free Determination of Protein-Ligand Equilibrium in Aqueous Solution using Overlayer Enhanced Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (OE-ATR-FTIR)**, ***T.C. Ruthenburg***, *S.S.N. Park, T.A. Aweda, C.F. Meares, D.P. Land*, University of California, Davis

Protein binding/affinity studies are often performed using Surface Plasmon Resonance techniques that don't produce much spectral information. Measurement of protein binding affinity using FTIR is traditionally performed using high protein concentration or deuterated solvent. By immobilizing a protein near the surface of a gold-coated germanium internal reflection element interactions can be measured between an immobilized protein and small molecules in aqueous solution. Using flow injection analysis the on and off rates of these interactions and dissociation constant for the system can be determined. The dissociation constant for the molecule Yttrium-aminobenzyl-DOTA binding to the antibody 2D12.5 system was determined.

Electronic Materials and Processing
Room: B1 - Session EM-WeA

Contacts, Interfaces, and Defects in Semiconductors
Moderator: K.L. Kavanagh, Simon Fraser University, Canada

2:00pm **EM-WeA1 Contact Resistance and Material Mixing at the Metal/Organic Interface**, ***Y.B. Kim***, *D. Jeon*, Seoul National University, South Korea

The properties of interface formed by depositing metal on an organic substrate is very different from those of an organic film deposited on a metal substrate, which is because metal atoms can easily penetrate into the loose organic substrate. The degree of mixing at the interface of metal-on-organic depends on the growth condition such as temperatrue and deposition rate. We have compared the morphology and the contact resistance of a Au electrode deposited on a pentacene film at room and liquid nitrogen temperature. The samples were prepared by thermally depositing two Au electrodes on a pentacene thin film. The resistance between the two Au electrodes was measured for different channel lengths between them so that the Au/pentacene contact resistance could be estimated by extrapolating the resistance curve to zero channel length. Figure 1 shows resistance vs channel length measured between two Au electrodes deposited at room and liquid nitrogen temperatures. For both samples, the resistance decreases with decreasing channel length. Between the two Au electrodes deposited at room and liquid nitrogen temperature, the latter yields smaller resistance and thus the smaller contact resistance when extrapolated. Atomic force microscopy revealed a much higher degree of interface mixing for Au deposited at room temperature. Interface mixing or alloying is a common method to make an Ohmic contact for the case of metal electrodes on Si. Our experiment implies that the same strategy may not be applicable to the case of metal electrodes on the organic substrates. The structural deformation of pentacene molecules seem to create traps rather than creating conductive channels. We performed Fourier transform infrared spectrascopy to check the amount of deterioration of pentacene molecules due to the Au deposition. For both liquid nitrogen temperature and room temperature deposition, the infrared peak intensity of pentacene decreased due to the Au deposition, but the peak intensity for the latter case decreased more. We will also discuss X-ray photoemission spectroscopy measurements.

2:20pm **EM-WeA2 Schottky Metal-GaN and AlGaN-GaN Interface Issues Critical to HEMTs**, ***P. Shah***, *I. Batyrev, M. Derenge, K. Jones*, US Army Research Laboratory

GaN devices promise advantages over other compound semiconductors including higher power amplification, increased linearity, and less temperature dependent degradation. But today current collapse, slow switching transients, and poor gain profiles are present and may be related to interface trap densities. To shed some light, we analyzed the interfaces found in GaN HEMTs and correlated results with amplifier performance characteristics and first principle atomic and electronic structure simulations.

MOCVD grown GaN Schottky diodes were mesa isolation etched, and KOH etched to remove Ga residue and surface defects. Then Ti/Al/Ti/Au Ohmic and Ni/Au Schottky contacts were deposited and annealed.

These blocked 340V in the off-state. KOH reduced surface roughness and improved the on-state performance (150mA at 3.5V in good devices). The undoped GaN layer had a free carrier concentration of $5x10^{16}$ cm^{-3} from CV measurements. The reverse bias exhibits a soft breakdown due to an initial depletion followed by a slower field spreading. For three devices, the forward (2V) and reverse leakage (-1 V) currents were (A) 45mA, 3.4x10^{-10}A, (B) 17mA, 2.0x10^{-9}A, and (C) 4 mA, 3.6x10^{-8}A. Comparing the ideality factors for the three devices over a voltage range of 0 to 0.5 V, device (A) exhibited no bumps between 0.1 and 0.4 V (n = 1.04 at 0.2 V) and a smooth transition into the series resistance region, device (B) exhibited a bump at 0.4V with a peak n= 4.3. Device (C) exhibited a bump at 0.1V with a peak n=2.08.

These ideality factor bumps were seen with GaAs Schottky diodes and linked to interface trap densities. Our conductance measurements gave corresponding trap densities 0.3 eV from the band edge of (C) 1.02x10^{12}, and (B) 7.9x10^{11} cm^{-2} eV^{-1}, and for (A) much less. Also, the interface trap time constants are (C) 97 ns and (B) 81.9 ns and for (A) much longer.

Our first-principle simulation model of a planar bonded metal-semiconductor interface included an inhomogeneity at the interface and semiconductor interface defect interactions with H atoms and OH radicals during KOH etching. We assume that N antisite defects are common defects in GaN causing point defect pinning. After KOH etching these defects are passivated by two hydrogen atoms forming complexes H-N(Ga)-H and OH-N(Ga)-OH. The complexes do not have dangling bonds and do not participate in hybridization with extended states of a metal. Formation of the complexes could improve the interface state associated electrical properties of the Schottky diode, smooth the GaN (0001) surface and remove oxides residues.

Vendor provided GaN HEMTs were similarly analyzed and will be discussed.

2:40pm **EM-WeA3 The Use of Simulations to Address Current Problems in Schottky Barrier Contacts**, ***S.E. Mohney***, *K. Sarpatwari, O.O. Awadelkarim, N.S. Dellas*, Pennsylvania State University **INVITED**

A combination of simulations and experiments often provides a powerful approach to address scientific and engineering problems. In this presentation, we describe two examples of research on contacts to semiconductors in which we use simulations to develop methods to analyze data collected from Schottky barrier contacts. In the first example, we present an approach to accurately extract the Schottky barrier height from an axial contact to a semiconductor nanowire. Modification of the method usually used to analyze current-voltage (I-V) data from microscale planar Schottky diodes is necessary because of the influence of the semiconductor nanowire surface adjacent to the Schottky barrier contact. Band-bending at this surface influences the shape of the depletion region at the metal/semiconductor interface and must be controlled. We accomplish this control with a wrap-around gate. By analyzing I-V data generated using a commercial device simulator, we identify a method to treat the data to accurately extract the Schottky barrier height. Using the same approach that worked well for the simulated data, we next analyze Schottky barrier contacts to silicon nanowires that we nanofabricated with wrap-around gates. In another investigation, we examine approaches to extract the Richardson constant from planar Schottky barrier contacts that contain nanoscale inhomogeneities. Using Tung's model for inhomogeneous Schottky barrier contacts, we generate simulated I-V data for contacts with inhomogeneities of different sizes, densities, and departures from the homogeneous background barrier height. Then we compare various published approaches for extracting the Richardson constant, identifying their strengths and weaknesses. This section of the presentation concludes with the recommendation of a new approach for treating experimental data, and the approach is demonstrated for Schottky barrier contacts to wide band gap semiconductors.

4:00pm **EM-WeA7 2009 AVS John A. Thornton Memorial Award and Lecture - Nanofabrication Chemistry: The Impact of Solid Interfaces**, ***F.A. Houle****, Fremont, California **INVITED**

The presence of an interface can impose distinct local conditions that can have an important influence on the outcome of a chemical reaction at a nanoscale level. Loosely, two broad types of phenomena can be identified. In one, the interface can serve as an impermeable structure that imposes concentration gradients on materials in contact with it, leading to measurably different chemistry than would occur in its absence. In the other, the interface can serve as a means of accelerating transport, building in significant blur to the contacted regions. Semiconductor fabrication processes are influenced by one or both, directly controlling how well methods developed for the microscale can be adapted to the nanoscale. Examples drawn from etching, deposition, photolithography and nanoimprint lithography will be discussed, illustrating some general principles that may potentially be used to advantage in materials nanoprocess design.

4:40pm **EM-WeA9 A Novel Route Towards Electrical Connection and Probing of Nano-scaled Devices on Semiconductor Surfaces**, ***J. Koeble***, *M. Maier*, Omicron NanoTechnology GmbH, Germany, *D. Jie, N. Chandrasekhar*, Institute of Materials Research and Engineering (IMRE), Singapore, *C. Joachim*, CEMES-CNRS, France

A major challenge in Nanotechnology is the incorporation of single nano-devices into larger integrated circuits. Although work on individual (and non-integrated) nano-structures such as molecules is intense, the question of their electrical connection with more than two probes (such as conventional SPM experiments) remains an open question. Established nano-lithography techniques such as EBL and FIB seem to not satisfy requirements for ultra clean and defined contact structures at the atomic scale. Traditional instrumentation for analysis is fundamentally limited: How to cover the dimensional range of an integrated circuit (mm) down to the atomic scale of a single molecule device and at the same time to have an adequate integrated navigation system? To meet these requirements, we have established and being advancing a new approach integrating SPM technology with high resolution electron microscopy: (1) Bridging dimensions by combined SEM (down to below 3nm resolution) and STM operation at the atomic scale; (2) Rapid SEM navigation of four local STM probes; (3) Individual probe fine positioning by high resolution STM imaging; (4) STM based probe approach for "soft-landing" of sharp and f-ragile probes and controlled electrical contact for transport measurements. To open a route for fundamental evaluation of the potential of single molecule devices, this instrumental technology is employed to establish electrical connection for local transport measurements. As a model system, we have chosen Au nano-islands on MoS_2. These islands represent contact pads, each electrically connected by an individual STM probe. As good band gap (approx. 1.3eV transverse gap) semiconductor, MoS_2 has the potential to sufficiently decouple those nano-structures electrically at low voltage. Those Au triangular nano-islands have a lateral size of typically 10-30nm and form an "atomically" ultra clean and defined metal-semiconductor interface. We present measurements that prove (1) SEM based navigation and STM based electrical contacting with a tip radius in the 10nm range: (2) reproducible Schottky like IV properties for the individual STM tip/Au nano-island/substrate contact; (3) surface conductance measurements with variable inter-island distance down to 17nm; (4) comparison with surface conductance measurements of the bare MoS2 substrate. We also show that the individual STM probe can be employed under SEM to manipulate those Au nano-islands [1] with high precision in order to generate arbitrary multi probe planar contact configurations.

[1]: J.S. Yang, D. Jie, N. Chandrasekar and C. Joachim J. Vac. Sci. Tech. B, 25, 1694 (2007).

5:00pm **EM-WeA10 Dynamic Imaging and Analysis of the Charge Trapping at the Metal-Organic Interface**, ***C. Kim***, *D. Jeon*, Seoul National University, South Korea

Understanding of metal/organic interfaces is one of the key issues for the design of high performence organic devices. We have studied the interface properties of the Al/pentacene/Au sandwich samples by performing electrostatic force microscopy (EFM) and measuring *I-V* curves at various temperatures. The Al/pentacene/Au sandwich sample showed a typical rectifying *I-V* curve as expected from the energy diagram. Interestingly, the current increased with time when a constant forward bias was applied. In order to understand the reason, we performed EFM of the cross section of Al/pentacene/Au to measure the time variation of the charge density across the interface. The result suggested that there was a charge accumulation at the Al/Pentacene interface and that the reason for the current increase with time was the lowered potential barrier caused by the trapped charges. From the temperature-dependent *I-V* measurement, we could estimate the amount of barrier lowering. When the measurement was performed in UHV environment, the current increase was not observed, which suggested that water molecules diffused into pentacene in the ambient condition played a role of trap sites.

5:20pm **EM-WeA11 Au-$Al_{0.27}Ga_{0.73}N$ Shottky Barrier Formation and Charge Carrier Mobility Estimation**, ***S. McHale***, Air Force Institute of Technology, *Ya. Losovyj*, Nebraska Center for Materials and Nanoscience, University of Nebraska-Lincoln and J. Bennett Johnston Sr. Center for Advanced Microstructures and Devi, *D. Wooten, J. McClory, J. Petrosky*, Air Force Institute of Technology

Au-AlGaN Shottky barrier formation is observed using Au evaporation on an $Al_{0.27}Ga_{0.73}N$ strained Wurtzite structure, thin film that is deposited on GaN. Low Energy Electron Diffraction was performed to verify the integrity of the Au deposition. Energy dependent, synchrotron generated photoemission spectroscopy ranging from 15 to26 eV under UHV conditions clearly determines a Fermi edge shift of up to 0.5 eV. Charge carrier mobility is inferred using valence band mobility edge data.

---

* John A. Thornton Memorial Award Winner

Energy Frontiers Research Centers
Room: A8 - Session EN-WeA

Energy Frontiers Research Centers
Moderator: E.S. Aydil, University of Minnesota

2:00pm **EN-WeA1 "Nano" Solutions to "Macro" Energy Problems**, ***V.I. Klimov***, Los Alamos National Laboratory **INVITED**

In this presentation, I will review some of our work on novel nanostructured materials and new nanoscale physical phenomena related to the problem of high-efficiency conversion of solar light into electrical or chemical energy. Specifically, I will discuss topics such as carrier multiplication (multiple exciton generation by single photons), plasmonic and photonic effects for improved light harvesting, and exploratory device structures comprising nanocrystal quantum dots. I will also give a brief overview of our newly funded Energy Frontier Research Center (EFRC) for Advanced Solar Photophysics where some of these problems are being tackled.

2:40pm **EN-WeA3 Understanding Charge Separation and Transfer at Interfaces in Energy Materials and Devices**, ***P.F. Barbara***, University of Texas, Austin **INVITED**

This seminar focuses on our recently constructed research program, selected for funding by the U.S. Department of Energy as an Energy Frontier Research Center (EFRC), that is uniquely well-suited to critically advance the fundamental understanding of interfacial charge separation and transfer processes in nanostructured organic photovoltaic (OPV) and electrical energy storage (EES) materials. Current limitations in the basic scientific understanding of charge separation and transfer processes in these materials represent a major scientific roadblock to achieving U.S. energy security. The mechanistic understanding of these processes in nanomaterials is in its infancy, without a broadly accepted theoretical description. Moreover, existing experimental tools and theoretical models are insufficient to definitively address the many outstanding scientific issues for the complex nanomaterials in this field. Instead, completely new multidisciplinary approaches, featuring greater molecular-level precision and accuracy and closer coupling between theory and modeling, are necessary to drive the fundamental aspects of this field forward. Therefore, we have constructed an EFRC research program that is based on two critical strategies: (i) We will support a set of coordinated research projects that study unique and novel interfacial prototypes that climb the ladder of molecular complexity from well-defined epitaxial crystal/crystal interfaces, through isolated crystal/crystal interfaces, to model polymer/crystal interfaces and then to actual OPV and EES devices. (ii) We will use powerful, state-of-the-art imaging and sub-ensemble methods (e.g., single particle spectroscopy and imaging) to make correlated measurements of structure and charge separation/transfer processes on the molecular scale for each type of interfacial prototype. Experimental data obtained by means of these two strategies will be modeled and analyzed by advanced theoretical and computational methods, leading to new insights on the molecular-level mechanisms of charge separation and transfer functions of complex OPV and EES nanostructured materials. This seminar will introduce the three major research thrusts of our EFRC (interfacial charge separation, interfacial charge transfer and Li^+-coupled charge transfer) and describe ongoing research projects within these three thrusts. If successful, this EFRC will produce three important outcomes: (1) new OPV and EES materials that are rationally designed to be substantially more efficient than current state-of-the-art materials; (2) a new suite of molecular-level tools to be used both in academia and in industry to evaluate and optimize these new molecular materials; and (3) the education of a new generation of energy researchers who are trained to produce these materials and utilize these molecular tools.

4:00pm **EN-WeA7 The Center on Nanostructuring for Efficient Energy Conversion (CNEEC) at Stanford directed by Stacey Bent and Fritz Prinz**, ***F.B. Prinz***, Stanford University **INVITED**

The center will identify ways in which high gradients, high surface to volume ratios and and low dimensionality can improve materials properties such as light absorption, charge transport, and catalytic activity.

This talk will outline strategies and plans for tuning thermodynamics/kinetics, photon management, and optimizing transport at reduced dimensions that may lead to improved photovoltaic devices, fuel cells, and batteries.

4:40pm **EN-WeA9 Excitonics**, ***M.A. Baldo***, Massachusetts Institute of Technology **INVITED**

Conventional electronic devices can be difficult to manufacture; their constituent materials require very high levels of order and achieving such low entropy in a semiconductor requires expensive and energy intensive fabrication. For example, the energy payback time for a crystalline silicon solar cell is on the order of 2 years, and at current manufacturing growth rates, it is expected to take at least 20 years to produce enough silicon-based solar cells to make a significant impact on the world energy supply.[1] Similarly, epitaxial growth constraints are likely to limit solid state lighting sources to a small fraction of the overall demand for lighting. There is an alternate approach that is more suitable for large scale production. In the new Energy Focused Research Center (EFRC) for Excitonics, we address materials with only short-range order. Such nanostructured materials are compositions of nano-engineered elements such as organic molecules, polymers, or quantum dots and wires, in films bound together by weak van der Waals bonds. These materials are characterized by *excitons* that are *localized* within the ordered nanostructures. Excitons provide a unique means to transport energy and convert between photons and electrons. Due to localization of excitons, the optical properties of the films are relatively immune to longer-range structural defects and disorder in the bulk. And in contrast with the painstaking growth requirements of conventional semiconductors, weak van der Waals bonds allow excitonic materials to be readily deposited on a variety of materials at room temperature. We address two grand challenges in excitonics: (1) to understand, control and exploit exciton transport, and (2) to understand and exploit the energy conversion processes between excitons and electrons, and excitons and photons.

References 1. Lewis, N. S. & Crabtree, G. (eds.) *Basic Research Needs for Solar Energy Utilization* (U.S. Department of Energy, http://www.sc.doe.gov/bes/reports/files/SEU_rpt.pdf, 2005).

5:20pm **EN-WeA11 Excitonic Charge Separation at Interfaces**, ***X. Zhu***, University of Texas, Austin **INVITED**

When a molecular or nano material is electronically excited by a photon, the Coulomb attraction between the excited electron and the hole gives rise to an atomic-H-like quasi-particle called an exciton. The bound electron-hole pair also forms across a material interface, such as the donor/acceptor (D/A) interface in an organic heterojunction solar cell; the results are charge-transfer (CT) excitons. In a conventional p-n junction cell, the exciton binding energy is very small and there is a built-in potential to ensure charge separation. In contrast, there is not a priori a built-in potential in an excitonic solar cell based on organic molecules, polymers, or inorganic quantum dots. In this talk, I will attempt to address key factors determining charge separation in two model systems: organic semiconductor interfaces and inorganic quantum dot/electron conductor interfaces. I will highlight the roles of excess electronic energy and strong electronic coupling in determining excitonic charge separation.

Muntwiler, M.; Yang, Q.; Tisdale, W. A.; Zhu, X.-Y. *Phys. Rev. Lett.* **2008**, *101*, 196403.

Zhu, X.-Y.; Yang, Q.; Muntwiler, M. *Acct. Chem. Res.* **2009**, *42*, published on web 04/21/09.

Williams, K. J.; Tisdale, W. A.; Leschkies, K.; Haugstad, G.; Norris, D. J.; Aydil, E. S.; Zhu, X.-Y. *ACS Nano* **2009**, 3, 1532-1538.

Tisdale, W. A.; Williams, K. J.; Timp, B. C.; Norris, D. J.; Aydil, E. S.; Zhu, X.-Y. *to be published.*

Graphene Topical Conference
Room: C3 - Session GR+AS-WeA

Graphene: Surface Characterization
Moderator: P. Sheehan, Naval Research Laboratory

2:00pm **GR+AS-WeA1 Tuning the Properties of Dirac Fermions in Graphene**, ***A. Lanzara***, University of California, Berkeley **INVITED**

Graphene, a one atom thick layer of carbon, the supposedly ideal Dirac material, has been under the radar of theorists and experimentalist for many decades. Although novel physical properties were envisioned, graphene, as any other 2D material, was presumed not to exist in its free state because of long wavelength fluctuations will easily destroy purely 2D membranes. The recent success in isolating a single sheet of graphene has certainly challenged this view. In this talk I will present our experimental work in this field using a combination of spectroscopic and microscopy tools. I'll present experimental evidence of what drives the stability of a graphene membrane and show comparison between exfoliated and epitaxial graphene. I will then discuss the nature of fermions in graphene sheets and how their peculiar electronic structure can be tuned by engineering small terraces of graphene down to nm size, where the physics gets dominated by quantum confinement. The implications of our study on the properties of Dirac materials and their potential role for applications are discussed

2:40pm **GR+AS-WeA3 Growth of Semiconducting Graphene on Pd(111)**, ***S. Kodambaka****, *S.-Y. Kwon*, University of California, Los Angeles, *C.V. Ciobanu*, Colorado School of Mines, *V. Petrova, J. Bareno,* University of Illinois, *V.B. Shenoy,* Brown University, *V. Gambin,* Northrop Grumman Space and Technology, *I. Petrov*, University of Illinois**INVITED**

We report *in situ* variable-temperature scanning tunneling microscopy studies of graphene growth on Pd(111) during ethylene deposition at temperatures between 723 and 1023 K. We observe the formation of monolayer graphene islands, 200-2000 Å in size, bounded by Pd surface steps. Surprisingly, the topographic image contrast from graphene islands reverses with tunneling bias, suggestive of a semiconducting behavior. Scanning tunneling spectroscopy measurements confirm that the graphene islands are semiconducting, with a bandgap of 0.3±0.1 eV. Using density functional theory calculations, we attribute this phenomenon to the breaking of hexagonal symmetry due to a strong interaction between graphene and the nearly commensurate Pd substrate. Our findings suggest the possibility of preparing semiconducting graphene layers for future carbon-based nanoelectronic devices via direct deposition onto strongly interacting substrates.

4:00pm **GR+AS-WeA7 Electronic Corrugation of Rippled Graphene Grown on Ru(0001)**, *B. Borca, S. Barja,* Universidad Autonoma de Madrid, Spain, *M. Garnica,* IMDEA Nanociencia, Spain, *J.J. Hinarejos,* Universidad Autonoma de Madrid, Spain, ***A.L. Vazquez de Parga***, *R. Miranda*, UAM & IMDEA Nanociencia, Spain

By means of Scanning Tunneling Microscopy/Spectroscopy (STM/STS) we investigate the electronic and structural modulation of epitaxial graphene grown on Ru(0001). The difference in lattice parameter between graphene and Ru(0001) induces in the graphene overlayer a Moiré pattern with hexagonal order and a lateral periodicity of around 3nm. The bonding with the substrate occurs through the hybridization of C *p*-states with Ru *d* states. Photoelectron spectroscopy shows that the bonding between the graphene and the metallic substrate is not carbidic and the graphene is doped with electrons from the substrate [1].

The hybridization between the carbon and ruthenium atoms changes inside the unit cell [2]. Measuring dI/dV maps we observe inhomogeneities in the charge distribution, i.e., electron pockets, in some areas of the ripples. This inhomogeneity can be understood with the help of a tight-binding model which incorporates a periodic potential associated with the structural ripples that induces a shift of the electronic levels and a corresponding charge transfer from conduction to valence bands for some atoms and the opposite in the others [3].

The influence of the modulated electronic structure in the STM images is quite strong. Large differences in corrugation values were measured in the STM images taken exactly in the same spot and changing the bias voltage applied between tip and sample. A compilation of data measured with different tips and different samples show that the apparent corrugation of the Moiré superstructure is essentially constant (0.1 nm) in the interval from -3V to -1V and diminish as the voltage goes from -1V up to +2V (0.03 nm). For a bias voltage higher than +2.5V, the contrast of the Moiré is inverted. By means of STS we measured, spatially resolved, the surface unoccupied density of states. The *d*I/*d*V spectra show that the contrast inversion is due to the presence of a strong peak at 3V above the Fermi level in the lower areas of the Moiré structure.

These results demonstrate that the electronic effects in this system are strong enough to overcome the actual geometric corrugation of the graphene layer.

[1] F. J. Himpsel *et al.*, Surf. Sci. Lett. **115,** L159 (1982)

[2] A.B. Preobrajenski *et al.*, Phys. Rev. B **78,** 073401 (2008)

[3] A. L. Vázquez de Parga *et al.,* Phys. Rev. Lett. **100,** 05680 (2008)

4:20pm **GR+AS-WeA8 Mapping the Geometric and Electronic Structures of Epitaxial Graphene**, *B. Wang,* ***M. Caffio***, *R. Schaub*, University of St Andrews, UK

A single layer of graphite is known as graphene [1]. It is acknowledged that graphene is a candidate for future electronic devices when supported. Hence a detailed understanding of its geometric and electronic properties is essential. Many studies have in common the observation of moiré superstructures with parameters depending on the mismatch between graphene and substrate [2]. However, an in-depth characterization of the monolayer and its interaction with the support has so far been hampered by experimental limitations, and is strongly debated. We report on a low temperature STM study of graphene grown by low-pressure CVD of ethylene on Rh(111). Topography measurements show that the C-Rh interactions lead to distortions of the ideal, free-standing graphene, resulting into two sets of superstructures: one is characterized by a coincidence lattice expanded to (12×12)/(11×11), while the other is contracted to (11×11)/(10×10). The coexistence of several graphene superstructures on a transition metal substrate is in contrast to previous reports. Both superlattices exhibit remarkable coherence lengths, in excess of 1000 nm. However, high-resolution images allow us to precisely monitor the registry of the C atoms with respect to the underlying substrate, revealing that the atomic arrangements are subject to local distortions. Resonance transmission microscopy and spectroscopy, in combination to DFT calculations, were further used to obtain deeper insight into the altering environment at the graphene/Rh(111) interface. Our results show how variations of the local work function within the overlayer unit cell provide invaluable information on the electronic coupling between graphene and Rh(111) substrate.

[1] K.S. Novoselov *et al*., Nature **438**, 197 (2005)

[2] J. Coraux *et al*., Nano Letters **8**, 565 (2008)

4:40pm **GR+AS-WeA9 Rotational Domains of Graphene on Ir(111)**, ***S. Nie***, *E. Loginova, K. Thürmer, N.C. Bartelt, K.F. McCarty*, Sandia National Laboratories

We use scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), and low-energy electron microscopy (LEEM) to study four different orientations of single-layer graphene sheets on Ir(111). The most-abundant orientation (R0) has been previously characterized in the literature [1]. While less prevalent than R0, the three additional structures can still occur as relatively large domains, tens of microns in spatial extent. We find that the four types of graphene differ simply in how the graphene sheets are oriented relative to the in-plane directions of the Ir lattice. That is, the four types of graphene are rotational variants, similar to the rotational variants of graphene on Pt(111) [2,3]. Using selective-area LEED, we find the graphene sheets in the other three variants to be rotated by approximately 14°, 18.5° and 30° (R30), respectively. The R30 structure is studied in detail with STM. Compared with the R0 structure, R30 has much less height corrugation. We propose atomic models for the new variants. The moiré structures can be classified using simple geometric rules involving the different periodic and quasiperiodic structural motifs. In addition, LEEM reveals that linear defects form in the graphene sheets during cooling from the synthesis temperature. STM shows that the defects are ridges where the graphene sheets locally delaminate as the Ir substrate contracts. We will describe the factors that control the relative abundance of the different variants.

[1] A. T. N'Diaye, J. Coraux, T. N. Plasa, C. Busse, and T. Michely, New J. Phys. **10**, 16 (2008).

[2] T. A. Land, T. Michely, R. J. Behm, J. C. Hemminger, and G. Comsa, Surf. Sci. **264**, 261 (1992).

[3] M. Sasaki, Y. Yamada, Y. Ogiwara, S. Yagyu, and S. Yamamoto, Phys. Rev. B **61**, 15653 (2000).

5:00pm **GR+AS-WeA10 Deposition and Characterization of HfO_2, Al_2O_3 and SiO_2 Dielectrics for Graphene-Based Devices**, ***A. Pirkle***, University of Texas at Dallas, *L. Colombo,* Texas Instruments Incorporated, *R.M. Wallace*, University of Texas at Dallas

We present a study of dielectric deposition on graphene and bulk graphite for nanoelectronic device applications. Recent studies have demonstrated that the chemically inert nature of the graphene surface presents challenges to uniform deposition of high quality dielectrics by conventional deposition techniques including ALD. These issues are compounded by the ultrathin nature of graphene, as any covalent bonding that disturbs the underlying graphene lattice is likely to induce scattering and degrade mobility.

In this study, Al, Hf and Si are deposited by electron beam evaporation and subsequently oxidized. We also examine deposition of dielectrics by reactive electron beam evaporation in the presence of a partial pressure of oxygen in the vacuum chamber. Chemical interactions with the substrate are analyzed by means of *in-situ* x-ray photoelectron spectroscopy (XPS) before and after oxidation. Any presence of carbide bonding (AlC, HfC, SiC) is likely to degrade mobility, and we examine the conditions under which carbide bonds are formed. The oxidized films are also characterized by *ex-situ* Raman spectroscopy, particularly with regard to the formation of D-band states that are indicative of damage to the graphene lattice during deposition or oxidation. Surface morphology of the deposited films is studied using atomic force microscopy (AFM), particularly with regard to uniformity as pertinent to thickness scaling.

This work is sponsored by the NRI SWAN center.

---

* Paul Holloway Award Winner

5:20pm **GR+AS-WeA11 Large Area Graphene Formed by the Catalytic Exfoliation of Natural Graphite with Invar Alloy**, ***J.C. Sung***, KINIK Company, Taiwan, *K. Chang, K. Hsu,* National Taipei University of Technology, Taiwan, *M. Sung*, Advanced Diamond Solutions, Inc.

Graphene is the ideal material for many dream applications, such as single electron transistors, field emission sources [1], light through electrodes, clothing solar cells, terra hertz surface acoustic wave (SAW) filters, wall paper displays, UV light emitting diodes, atomic gas sensors, DNA or antigen wafers…etc. However, a practical method to fabricate meter-sized graphene is still beyond imagination. We made use the mechanism of diamond synthesis in liquid phase and produced graphene of several hundreds microns. Such graphene revealed silk-like tenderness with transparent folding lines. This promising process appears scalable for making device-sized graphene in the near future. This paper also presented many intriguing aspects related to the growth of large graphene. We also proposed a new hypothesis of graphene formation by the catalytic exfoliation of graphite in molten iron group alloys.

Inkjet Technology: Printing, Materials Processing, and Microfluidics Fundamentals Topical Conference
Room: B3 - Session IJ+MN+TF-WeA

Inkjet Printing Technology: Advances and Challenges
Moderator: D.P. Trauernicht, Eastman Kodak Company

2:00pm **IJ+MN+TF-WeA1 Scaling Inkjet Printing to Nano Dimensions**, ***J. Bokor***, University of California, Berkeley **INVITED**

For many applications of inkjet printing, scaling the droplet size, and hence the resolution of printed features to micro and even nanoscale dimensions would be of great benefit. I will describe work on scaling a thermal printhead technology to droplet diameter in the range of one micron (0.5 femtoliter). Prospects for further scaling to nanodimensions will also be discussed.

2:40pm **IJ+MN+TF-WeA3 The Technology and Capabilities of Thermal Inkjet Printing**, ***E.G. Hanson***, Hewlett-Packard Laboratories **INVITED**

Thermal ink jet (TIJ) technology has a wide range of capabilities in the non-contact dispensing and printing of materials. TIJ is best known as an extremely effective and successful method for printing of documents and images on paper, using colored inks, but its applications extend far beyond ink-on-paper.

A TIJ printhead is a MEMS (Micro Electro Mechanical System) device, incorporating electronic devices and micro-machined geometrical features which are fabricated on a silicon wafer. TIJ excels in scalability and nozzle packing density. Over the past 20 years, its performance in terms of ejected ink drops per second per printhead has doubled every 18 months.

TIJ technology is extremely precise, offering volumetric control as low as 1% coefficient of variation for volumes > 0.1 microliter, and placement accuracy as low as 3 micrometers standard deviation. A wide range of materials can be ejected very effectively, including nanoparticle suspensions, pharmaceutical compounds, bioactive molecules, polymers, and adhesives. In addition to aqueous solutions, TIJ can efficiently jet numerous non-aqueous solvents.

TIJ is a drop-on-demand ink jet technique, meaning that ink drops are only ejected from nozzles when needed. In contrast, continuous ink jet technology generates a steady-state stream of ink drops, using additional components downstream of the nozzles to deflect and recirculate those drops which are not needed. Aside from TIJ, there is one other common type of drop-on-demand ink jet: piezoelectric (piezo) ink jet. In both TIJ and piezo devices, ink is ejected from nozzles when needed by applying pressure pulses to fluid-filled chambers upstream of those nozzles. These two ink jet techniques use different pressure pulse generation methods – formation of a vapor bubble inside the chamber in the case of TIJ, and mechanical deflection of a diaphragm in the case of piezo. TIJ uses much smaller chambers and generates much higher peak pressures than piezo, giving advantages in nozzle packing density, low printhead cost, and high tolerance to trapped bubbles. Piezo printheads are larger, higher cost, and more sensitive to trapped bubbles, but they do also offer longer printhead life and a wider fluid space than TIJ.

A large variety of materials deposition and dispensing applications are benefiting from the high precision and versatility of TIJ technology. The base technology of TIJ was primarily developed originally for the large market of printed ink on paper, but now these materials applications are leveraging and extending that technology base.

4:00pm **IJ+MN+TF-WeA7 Recent Advancements in Continuous Inkjet Technology**, *J. Chwalek, E. Furlani, J. Gao, K. Vaeth,* Eastman Kodak Company, *G. Hawkins,* Eastman Kodak Company (retired), ***J.M. Grace***, Eastman Kodak Company **INVITED**

Recent advancements at Eastman Kodak Company in the ability to precisely control the instabilities in thermally stimulated microjets, coupled with advancements in MEMS technology, computer modeling of complex microfluidic systems, nanopigment ink technology, and ink-substrate interactions, enabled the development and subsequent commercialization of a new continuous inkjet technology. This technology offers extremely high productivity with high image quality and excellent reliability on a wide variety of substrates while maintaining a low total ownership cost. This technology, referred to as KODAK Stream Inkjet Technology (or "Stream"), forms the basis of a technology platform that is highly extensible, allowing participation in markets that rely up on high-speed digital print production. The fundamental physics of droplet generation and control and nanopigment ink chemistry create inherent advantages in areas such as productivity, image quality, and ink latitude. In this presentation, we will describe the principles of operation of Stream 's printhead. These principles include the physics of droplet formation, a discussion of fluid properties relative to jet modulation, wavelength dependencies, thermal modulation schemes, satellite drop formation, and drop control effects.

4:40pm **IJ+MN+TF-WeA9 Innovative Strobe-Based System for Analysis of Drops-in-Flight**, *K. Johnson, Y. Kipman,* ***G. Bartos***, ImageXpert Inc.

Imaging and measurement of drops-in-flight often relies on the measurement system's ability to drive the print head directly in order to synchronize the strobe for repeatable image capture. In addition, many systems do not have the necessary combination of precise strobe control, camera triggering, and powerful image analysis for full drop-in-flight evaluation.

This paper includes a discussion of a fully integrated machine-vision based system for visualization and measurement of drops-in-flight that can be used with any frequency-based jetting system. The strobe is linked to the firing frequency of the print head, so while it is synchronized, it is independent of the specific print head being used.

The imaging system resolves droplets down to 3 picoliters in volume at the highest zoom level. And an open architecture software package allows for image collection and archiving as well as powerful and flexible image analysis.

This paper will give an overview of the details of this system as well as show some of the system capabilities through several examples of drop-in-flight analysis.

5:00pm **IJ+MN+TF-WeA10 Controlling the Evaporation and Material Deposition Process of Printed Drops by Systematic Substrate Modification**, ***V. Bromberg***, *S. Gawande, T. Singler, Y. Sun*, Binghamton University

The evaporation dynamics of an inkjet-printed drop on a solid surface have been investigated experimentally. An inkjet-printed drop will generally evaporate in two modes – a continuous decrease in contact angle with a constant contact area, followed by a shrinking of the contact area at a constant contact angle. This evaporation process determines the internal flow and final deposition pattern of functional material being carried by the drop. In an effort to better understand this process, fluorescent microscopy was used to visualize the flow of colloidal material inside printed water drops. We have systematically examined the effects of substrate wettability in controlling the flow and deposition dynamics. It has been found that critical wettability values (as determined by the contact angle) exist which delineate the evaporation and deposition process into regimes of significantly different final deposit patterns. These critical values have been explored as functions of particle characteristics (volume fraction, surface functionality, size) and ambient conditions (relative humidity). A theory of particle kinetics within the three-phase contact line region has been proposed to explain the existence of these critical wettability parameters. These parameters have been used to suggest effective techniques for controlling the shape and structure of final deposition for inkjet printing functional material.

5:20pm **IJ+MN+TF-WeA11 Droplet Velocity Fluctuations in Thermally Stimulated Continuous Liquid Jets: Assessing the Effects of Nozzle Bore Geometry**, ***J.M. Grace***, *G. Farruggia*, Eastman Kodak Company

The break-up of thin liquid jets into droplets, known and studied for over a century, has significant practical applications, including inkjet printing. Whether jets are stimulated in on-demand or continuous modes, noise in the stimulation and break-up process can generate fluctuations in drop velocity. As inkjet technology continues to advance to higher resolution and the requirements for control of drop placement become increasingly more stringent, the fundamental noise characteristics of the break-up process become of increasing interest. In this presentation, we study the spatial jitter of drops to infer the underlying velocity fluctuations in thermally stimulated continuous fluid microjets. We present measurements of jitter for fluids jetted from nozzles having different bore radii and bore lengths. The jitter appears to decrease for decreasing nozzle bore lengths. Analysis based upon observed break-off lengths and the implied initial radial perturbations of the jet is presented as a means to assess whether nozzle bore geometry has a fundamental effect on jitter. In addition, analysis based upon energy delivered to the jet during each drop formation period is presented to assess the importance of thermal coupling between heater and jet.

5:40pm **IJ+MN+TF-WeA12 Novel Dynamic Volume Control in Jetting of Complex Fluids**, ***G.E. Mårtensson***, *W. Holm*, Mydata Automation AB, Sweden

In conventional ink jetting applications, a pressure difference is used to ensure the continuous and prompt filling of the jetting chamber between jetting actuations. The delivery of precise fluid volumes utilizing inkjet-like drop-on-demand jetting technology is primarily controlled by the piezo voltage that actuates the jetting chamber (Gerhauser et al. 1983, SID 83 Digest). The jetting of large volumes, in excess of 1 nL, of complex viscous fluids is complicated by the difficulty of filling the ejection chamber quickly after the previous droplet ejection.

In order to ensure the delivery of fluid to the ejection chamber, a mechanism utilizing a helical viscous pump has been introduced and implemented by the authors. The fluid is fed to the helical pump from a reservoir of fluid stabilized by a regulated reservoir pressure. The flow rate is regulated by the speed of the driving surface of the viscous pump. The ejection mechanism consists of a piezo actuated piston that drives the fluid in the chamber through the nozzle on to the intended surface.

The ejected volume of fluid has been studied with respect to piezo voltage, V_p , pulse time, t_p , of the piezo signal and the angular speed of the helical viscous pump. The ejected volume has been estimated from digital photographs taken of the droplet, as well as via 3D profilometry methods. It has been shown in the experimental jetting setup that the volume of a jetted deposit is only affected to a minor degree, of the order of 5% of the goal volume, by the chosen piezo voltage, V_p , acting on the piston. This is also true for the chosen pulse time, t_p . The form of the ejected fluid droplet is affected by the pulse time, tp, only for relatively small volumes. Through imaging experiments, it has been shown that the speed of the ejected droplet has a nearly linear response to the piezo voltage, V_p .

The effect of the fluid's viscosity, represented by its dynamic shear modulus, G*, and its dependancy on rate of shear, $d\gamma$ / dt , on the ejected volume was also studied. The effect on the delivered volume was slight for the range of non-Newtonian fluids available, in spite of a strong shear-thinning behaviour.

Magnetic Interfaces and Nanostructures
Room: C1 - Session MI+EM-WeA

Magnetism and Spin Injection in Semiconductors
Moderator: Y.D. Park, Seoul National University, South Korea

2:00pm **MI+EM-WeA1 Anomalous Nernst Effect in $Ga_{1-x}Mn_xAs$ Ferromagnetic Semiconductors**, ***J. Shi***, University of California, Riverside **INVITED**

The origin of the anomalous Hall effect (AHE) in ferromagnets has been a subject of long-standing debate. Dilute magnetic semiconductors (DMS) provide an excellent test ground for clarifying the issues. In our study, we engineered a series of GaMnAs thin films with different doping levels and with perpendicular magnetic anisotropy which allows us to investigate both electrical and thermoelectric transport properties at zero magnetic field. Both Seebeck and Nernst coefficients (S_xx and S_xy) were measured simultaneously with the longitudinal and transverse resistivities (rho_xx and rho_xy). In addition to an usually large spontaneous or anomalous Nernst effect (ANE), we also found that both AHE and ANE arise from the same physical origin. When the temperature is varied, although the sign of AHE (rho_xy) remains unchanged, the sign of ANE (S_xy) switches at an intermediate temperature below Tc. Furthermore, we found that the same Mott relation which links the electrical conductivity and thermoelectric coefficients works very well for the anomalous transport. A simple Mott relation analysis rules out the extrinsic skew-scattering mechanism immediately with the sign change in S_xy. A further quantitative analysis of the overall temperature dependence yields exponent n=2 in rho_xy ~ rho_xx^n, indicating that the intrinsic spin-orbit effect is likely responsible for both AHE and ANE.

2:40pm **MI+EM-WeA3 Local Structure of Cr in the Epitaxial Ferromagnetic Semiconductor Cr-doped Ga_2Se_3/Si (001)**, ***E. Yitamben****, *T.C. Lovejoy, A. Pakhomov*, University of Washington, *S. Heald*, Argonne National Laboratory, *F.S. Ohuchi, M.A. Olmstead*, University of Washington

The III-VI compound Ga_2Se_3 is an intrinsic vacancy semiconductor which not only can be grown epitaxially on silicon, but, once doped with a transition metal, presents interesting potential for application in spintronics devices, since we have found it to be ferromagnetic at room temperature. Unlike III-V or II-VI materials, the intrinsic vacancies in Ga_2Se_3 create both multiple sites for dopant incorporation, raising the possibility of separate control of magnetic and carrier doping, and anisotropic band-edge states, which may increase both the Curie temperature and the magnetic anisotropy. This work presents experimental investigations of Cr-doped Ga_2Se_3 epitaxially grown on Si(100):As that probe interactions among structure, carriers and magnetism in this new class of dilute magnetic semiconductors.

Inclusion of a few atomic percent Cr into the Ga_2Se_3 lattice results in laminar semiconducting films that are ferromagnetic at room temperature, with a magnetic moment of 4 μ_B per Cr in 6 nm films, and 40% lower in 20 nm films. X-ray absorption and photoemission measurements reveal Cr in an octahedral environment; X-ray and low energy electron diffraction reveal a cubic structure with lattice constant close to that of the underlying silicon. This is surprising, since both the vacancies and Ga cations occupy tetrahedral sites in pure Ga_2Se_3.

Above ~6%, scanning tunneling microscopy (STM) reveals the formation of islands within trenches whose shape and size depend on the Cr concentration and whether or not a Ga_2Se_3 buffer layer is deposited first. The islanded films also exhibit room temperature ferromagnetism, though with about half the magnetic moment per Cr. Unlike low concentration films, they are metallic rather than semiconducting.

Acknowledgments: This work is funded by the NSF Grant DMR-0605601, NSF NER-0508216

3:00pm **MI+EM-WeA4 Ferromagnetism in Gd- and Si-co-implanted GaN**, *R. Davies, B. Gila*, ***C. Abernathy***, *S.J. Pearton, C. Stanton*, University of Florida

Ion implantation has been studied as a magnetic ion incorporation method in semiconductor materials for spintronic applications due to excellent control over the amount of the implanted ion and the resultant magnetic properties of the implanted material. GaN thin films grown via metal-organic chemical vapor deposition (MOCVD) were co-implanted with Gd^+ ions with an energy of 155 keV and dose of 2.75×10^{10} cm^{-2} and Si^{4+} ions with energies of 5 keV and 40 keV and corresponding doses of 8×10^{11} cm^{-2} and 3.6×10^{12} cm^{-2}. Before annealing, x-ray diffraction measurements revealed that the implanted GaN thin films exhibited no secondary phase formation or clustering effects attributable to Gd. Superconducting quantum interference device (SQUID) magnetometer measurements indicated that a Gd- and Si-co-implanted GaN thin film exhibited about an order of magnitude higher magnetic moment than a Gd-implanted GaN thin film. Both of these thin films displayed ferromagnetic ordering and Curie temperatures above room temperature. The co-implanted GaN thin film also demonstrated a larger magnetic moment than a Gd- and Si-co-doped GaN thin film grown via molecular beam epitaxy (MBE) while possessing a smaller Gd concentration. The orientation of the applied magnetic field with respect to the thin film surface was seen to have an effect on the measured magnetic properties of the thin films. This orientation dependence may help elucidate the relationship between the defects produced by the implantation process and the ferromagnetic ordering exhibited by these materials.

4:00pm **MI+EM-WeA7 Structural and Electronic Properties of EuO and Gd-doped EuO Films Prepared Via Pulsed Laser Deposition**, *X. Wang, K. Fox, W. Wang*, ***J. Tang***, University of Wyoming, *M.J. An, K. Belashchenko, P.A. Dowben*, University of Nebraska-Lincoln

Methods to prepare EuO thin films reported in the literature include reactive thermal evaporation of Eu in the presence of oxygen gas and molecular beam epitaxy (MBE). We have successfully prepared single phase polycrystalline and epitaxially grown EuO and Gd-doped EuO via pulsed laser deposition (PLD) using metal targets. This opens a new route to the preparation of this interesting material with high quality. Samples prepared in vacuum exhibit the typical M(T) curve for a ferromagnet and have a Curie temperature of 70 K. When the samples were grown under ultrahigh purity H_2 flow, they show the "double-dome" feature characteristic of

---

* Falicov Student Award Finalist

oxygen deficient EuO. Tc as high as 150 K has been observed for EuO. The increased Curie temperature is attributed to the magnetic coupling enhanced by the 4f-5d coupling between the Eu moments and doped electrons. Our results reaffirm that oxygen vacancies alone can substantially increase the Tc. Calculations on the phase diagram (for Gd+EuO), the effects of oxygen vacancies and associated band structures and density of states will be presented.

4:20pm **MI+EM-WeA8 Magnetic Molecules on GaN: A Low Temperature STM Investigation**, ***K. Clark***, *D. Acharya, V. Iancu, E. Lu, A. Smith, S.-W. Hla*, Ohio University

Spin electron interactions involving magnetic molecules and semiconductor surfaces are of great interest for the development of molecular spintronic devices. Due to its wide range of applications, GaN (0001) surface has received a special attention for the development of novel electronic devices. Here, we studied electronic and structural properties of TBrPP-Co molecules deposited on a freshly grown nitrogen polar GaN (0001) surface using a scanning tunneling microscopy and spectroscopy at 4.6 K under an ultra-high-vacuum condition. The TBrPP-Co molecule has a spin-active cobalt atom caged at the center of porphyrin unit and four bromo-phenyl groups are attached to its four corners. On GaN(0001), the molecules bind the surface via two molecular conformations: saddle and planar. In saddle conformation, the central part of the molecule is bent by lifting the two pyrrole units of the porphyrin macrocycle. STM images shows various self-assembled clusters of molecules on GaN(0001) surface. Within the self-assembled molecular clusters, the molecules are aligned either parallel or 90 degree rotated to each other. In the presentation, we will discuss the spin-electron coupling of this molecule-surface system. This work is supported by the Ohio University BNNT, NSF-PIRE: OISE 0730257, NSF-EMT: CCF-0622158, and the United States Department of Energy, DE-FG02-02ER46012 grants.

4:40pm **MI+EM-WeA9 Electrical Injection, Detection and Modulation of Spin Currents in Silicon**, ***O.M.J. van 't Erve***, *C. Awo-Affouda, A.T. Hanbicki, M.A. Holub, C.H. Li, P.E. Thompson, B.T. Jonker*, Naval Research Laboratory **INVITED**

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. Significant progress has recently been made on spin injection into the technologically important semiconductor, Si, using vertical device structures. Here we will present the electrical injection, detection and magnetic field modulation of lateral diffusive spin transport through silicon using Fe/Al2O3 surface contacts. The tunnel 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 up to 125 K demonstrate that the spin current can be modulated by a perpendicular magnetic field, which causes the electron spin to precess and dephase in the channel during transport. By changing the bias on the injector contact we can either inject or extract spin from the Silicon channel. Here we will show using Hanle and lateral spin-valve measurements that we can change the polarization of the spin accumulation by going from the injection regime to the extraction regime and we will compare the efficiency of spin-injection versus spin extraction.

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.

5:20pm **MI+EM-WeA11 Order From Chaos: α-Fe(001)/GaAs(001)**, ***J.G. Tobin***, *S.W. Yu,* Lawrence Livermore National Laboratory*, S.A. Morton,* Lawrence Berkeley National Laboratory*, G.D. Waddill,* Missouri University of Science and Technology*, J.D.W. Thompson, J.R. Neal, M. Spangenburg, T.H. Shen*, University of Salford, UK

For many years, the technological possibilities of spintronic or magneto-electronic devices [1], particularly when coupled with potentially pure spin sources such as half-metallic ferro-magnets, [2] have engendered great interest. Despite the limitations encountered in such potential sources [3], there is still ample reason to pursue such concepts. This is because, in part, even with sources that operate below 100% polarization, technologically important devices should emerge. [1] However, the challenges of device integration remain significant even for cases with lowered expectations, because often the physical realities of intermixing, disorder and alloying can creep into the attempts to fabricate structures based upon ideal conceptual designs. Within this context, ferromagnetic-semiconductor interfaces are potentially important for the future applications of spintronic devices. One possibility for a room temperature spin injector is Fe/GaAs. The growth of Fe upon GaAs(001) has been studied with Photoelectron Spectroscopy (PES), including Spin-Resolved PES . Despite evidence of atomic level disorder such as intermixing, [4] an over-layer with the spectroscopic signature of α-Fe(001), with a bcc real space ordering, is obtained. The results will be discussed in light of the possibility of using such films as a spin polarized source in device applications. Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. Work that was performed by UMR personnel was supported in part by the Office of Basic Energy Science at the U.S Department of Energy. Work that was performed by LLNL personnel was supported in part by the Office of Basic Energy Science at the U.S Department of Energy and Campaign 2 of WCI at LLNL. We would also like to thank J.A.D. Matthew, D. Greig, A.E.R. Malins, E.A. Seddon, and M. Hopkinson for their help with this project.

References
1. G.A. Prinz, Science 282, 1660 (1998).
2. R.A. de Groot, F.M. Mueller, P.G. van Engen and K.H.J. Buschow, Phys. Rev. Lett. 50, 2024 (1983).
3. P. Dowben, J. Phys. Condensed Matter 19, 310301 (2007).
4. J.D.W. Thompson, J.R. Neal, T.H. Shen, S.A. Morton, J.G. Tobin, G.D. Waddill, J.A.D. Matthew, D. Greig, and M. Hopkinson, J. Appl. Phys. 104, 024516 (2008) and references therein.

5:40pm **MI+EM-WeA12 Enhancement of Spin Injection Efficiency by Interface Modification for Fe and $Fe_{31}Co_{69}$ Thin Films on GaAs(001)**, ***S.F. Alvarado***, *G. Salis, A. Fuhrer, L. Gros, R.R. Schlittler*, IBM Zurich Research Laboratory, Switzerland

We report on a detailed study of the influence of ferromagnet/semiconductor interface modifications on the electrical spin injection efficiency of Fe and $Fe_{31}Co_{69}$ thin film electrodes into the GaAs(001) surface. These modifications are induced by: a) Varying the As/Ga surface concentration of GaAs(001); and b) Post-growth annealing of the ferromagnetic thin films. Electrical spin injection experiments are carried out in a non-local device geometry at temperatures between 2.5 and 300 K. Devices were fabricated by means of either optical, e-beam, or nanostencil lithography. Non-local spin signals in the range of 2V/A at a temperature of 5K have been detected between two strip electrodes, one 2 and the other 6 µm in width, 60 µm long, separated 3 µm from each other. The spin-polarization characteristics of the devices are observed to strongly depend on substrate surface preparation and annealing treatment of the metal/semiconductor devices. The latter has a very strong influence on the magnitude of the non-local spin polarization signal, which we observe to increase by about two orders of magnitude after annealing steps from 120 °C up to 290 °C.

Nanometer-scale Science and Technology
Room: L - Session NS-WeA

Nanotubes - Electronics and Functionalization
Moderator: E.I. Altman, Yale University

2:00pm **NS-WeA1 Chemical and Biological Functionalization of Carbon Nanotubes**, ***S.S. Wong***, SUNY Stony Brook and Brookhaven National Laboratory **INVITED**

In the first part of the talk, we update covalent chemical strategies commonly used for the focused functionalization of single walled carbon nanotube (SWNT) surfaces. In particular, we explore advances in the formation of nanotube derivatives that essentially maintain and even enhance their performance metrics after precise chemical modification. We especially highlight molecular insights (and corresponding correlation with properties) into the binding of functional moieties onto carbon nanotube surfaces. Controllable chemical functionalization suggests that the unique optical, electronic and mechanical properties of SWNTs can be much more readily tuned than ever before with key implications for the generation of truly functional nanoscale working devices.

In the second part of the talk, we investigate the biocompatibility, specificity, and activity of a ligand-receptor-protein system covalently bound to oxidized SWNTs as a model proof-of-concept for employing such SWNTs as biosensors. In the third part of the talk, we describe a novel SWNT-based tumor-targeted drug delivery system (DDS) which has been developed, consisting of a functionalized SWNT linked to tumor-targeting modules as well as prodrug modules. There are three key features of this nanoscale DDS: (a) use of functionalized SWNTs as a biocompatible platform for the delivery of therapeutic drugs or diagnostics, (b) conjugation of prodrug modules of an anticancer agent (taxoid with a cleavable linker) that is activated to its cytotoxic form inside the tumor cells upon internalization and *in situ* drug release, and (c) attachment of tumor-recognition modules (biotin and a spacer) to the nanotube surface.

2:40pm **NS-WeA3 Carbon Nanotube-Based Biosensor for Detection of MicroRNA**, ***V.Z. Poenitzsch****, T. Booker, A. Clark, N. Nitin*, Southwest Research Institute

Carbon nanotubes (CNT) – field effect transistor (FET) sensors are promising candidates for label-free, sensitive detection of biological molecules. In this study, we have developed a proof-of-concept biosensor for the detection of microRNA (miRNA) in which designer oligonucloetide (ODN) probes covalently attached to CNTs serve as a highly specific molecular recognition function and FET device that translate changes in CNT electric properties serves as a signal transduction function. MicroRNA-21 was selected in this study as a model miRNA molecule. Basic research has shown that over-expression of miRNA-21 is associated with development of leukemia, breast cancer and prostate cancer. CNTs were functionalized with designer oligionucleotide (ODN) probes having conformational structures and sequences that are highly specific for hybridization with target miRNA-21. Conjugation of ODN probes with CNTs was examined using zeta potential surface charge measurements, fluorescent labeling, and atomic force and scanning electron microscopies. Biological activity and hybridization of immobilized ODN probe with miRNA 21 were further monitored using quartz crystal monitor measurements and fluorescent labeling. Subsequently, CNT-ODN network films were deposited using dielectrophoretic technique. Thin and wide metal electrodes that allow for increased Schottky contact areas were fabricated by magnetron sputter deposition of metals for source and drain electrodes using a shadow mask and tilted angle. Electrical impedance spectroscopy and current-gate voltage measurements were used to study the effect of ODN attachment and hybridization event on CNT electronic properties. In this presentation, we will discuss the fabrication and characterization of the developed sensor along with challenges of meeting the required specificity and sensitivity for real-world applications such as in vitro medical diagnostics.

3:00pm **NS-WeA4 Effect of Carboxy-Functionalized Multiwall Carbon Nanotubes on the Conductivity Performance of Tricomponent LBL Films**, ***X. Gu****, D.B. Knorr,* University of Washington*, G. Wang,* Tongji University, China*, R.M. Overney*, University of Washington

Lithium batteries offer high energy density, a flexible, lightweight design and longer lifespan than competing battery technologies. Poly(ethylene oxide) (PEO) is a polymeric material which has extensively been adopted as an electrolyte component in solid state rechargeable lithium batteries. PEO exhibits good complexation properties and high flexibility and retains good mechanical stability at temperatures up to its melting point. Recently, a layer-by-layer (LBL) technique was introduced to prepare battery thin films. This method offers fine control and tunability of material properties and architecture at the nanometer scale, and is a relatively simple method to implement. Films were fabricated by alternating deposition of PEO and poly(acrylic acid) (PAA) layers from aqueous solutions, However, PEO/PAA layer-by-layer (LBL) films exhibit low ionic conductivity when dry, and thus the inhibition of PEO crystallinity alone is not sufficient to improve the ionic conductivity. To achieve more enhanced conductivity in PEO films, various methods have been introduced. The exceptional electronic properties of carbon nanotubes (CNTs) have prompted intensive studies of PEO/CNTs composites. However, at present, these composites have shown only a moderate conductivity enhancement. LBL assembly has shown for other polymers to allow for excellent control of thickness and composition and diminished phase segregation compared with other methods of construction of CNT composites.

In this work, we demonstrate that fabrication of LBL films with carbon nanotubes is possible in a complex tricomponent film of PEO, PAA, and carboxy-functionalized multiwall carbon nanotubes (MWNT-COOH). Successful incorporation of carbon nanotubes layers and excellent surface coverage was observed by AFM topography images and lateral force microscopy. Our system displayed fast growth of LBL assembled films in the deposition process with film thicknesses reaching 1 mm for films composed of 10 cycles of layers. Rapid growth of the films affords fast preparation of PEO/PAA LBL films with incorporated carbon nanotubes which is essential for battery application. Impedance measurements and electrostatic force microscopy (EFM) were used to analyze the differences in ionic conductivity before and after incorporation of MWNT-COOH in to PEO/PAA assemblies. As expected, conductivity improved with the incorporation of the MWNT-COOH treatment. To this end we also employed thermomechanical characterization techniques including shear-modulation force microscopy (SM-FM) to investigate molecular mobility in the tricomponent systems.

4:00pm **NS-WeA7 Graphene Chemistry**, ***R.C. Haddon***, University of California, Riverside **INVITED**

We have recently demonstrated the high density functionalization of epitaxial graphene wafers with nitrophenyl groups.[Bekyarova, E.; Itkis, M. E.; Ramesh, P.; Berger, C.; Sprinkle, M.; de Heer, W. A.; Haddon, R. C., Chemical Modification of Epitaxial Graphene: Spontaneous Grafting of Aryl Groups. *J. Am. Chem. Soc.* **2009,** 131, 1336-1337] The chemical formation of covalent carbon-carbon bonds involving the basal plane carbon atoms offers a versatile approach to the control of the electronic properties of graphene; the transformation of the carbon centres from sp^2 to sp^3 introduces a barrier to electron flow by saturating the carbon atoms and opening a band gap which allows the generation of insulating and semiconducting regions in graphene wafers. This prototype chemistry when applied to carbon nanotubes allowed both covalent and ionic modification of the electronic structure; covalent attachment of functional groups was shown to transform the metallic single-walled carbon nanotubes into semiconductors.

In this talk I will discuss our recent results on the electronic and magnetic properties of chemically modified graphene and its relationship to single walled carbon nanotubes.

4:40pm **NS-WeA9 Spectroscopic Study of the Electron Transport Suppression Phenomenon in Carbon Nanotubes Field-Effect Transistors**, ***F. Lapointe***, Université de Montréal, Canada*, C.M. Aguirre,* École Polytechnique de Montréal, Canada*, P.L. Lévesque,* Université de Montréal, Canada*, P. Desjardins,* École Polytechnique de Montréal, Canada*, R. Martel*, Université de Montréal, Canada

Carbon nanotubes field-effect transistors (CNFETs) were thought to exhibit exclusive hole transport under ambient atmosphere because of the high potential barrier to electron injection at the electrode-nanotube contact interface. This hypothesis did not hold against a set of new experiments we devised, where ambipolar transport was observed under ambient atmosphere by merely changing the nature of the dielectric used as the substrate. Using controlled atmosphere experiments, we pinpointed the phenomenon responsible for the inhibition of electron transport in CNFETs, and showed it is mainly caused by an electrochemical charge transfer to the aqueous oxygen redox couple. We postulated that intermediates of the redox charge transfer are stabilised at the SiO_2 surface as charged oxygen species leaving a net negative charge at the surface and thus screening the applied gate potential. Focusing on a spectroscopic investigation, we tested the existence of these species. Thermodesorption spectroscopy experiments coupled to reflection-absorption infrared spectroscopy under high vacuum conditions were used to probe the dielectric interface of CNFETs operated under ambient atmosphere prior to insertion into the experimental chamber.

5:00pm **NS-WeA10 Direction Control of Carbon Nanotube Growth on Corrugated Patterned SiO_2 using Casimir Force and its Application to High Current FET**, ***K. Matsumoto****, S. Iwasaki, T. Kamimura, K. Inoue, T. Kishimoto, Y. Ohno, K. Mehashi*, Osaka University, Japan

The direction control of the carbon nanotube(CNT) growth on the SiO_2/Si substrate was first succeeded in at our will using the attractive force of "Casimir force" which concentrates at the upper edge of the corrugated pattern. By applying the present technique for CNT FET, the drain current was enhanced more than 10 times than the conventional CNT FET because of the effective bridging of CNTs between the source and drain electrodes.

The process for the direction control of CNT growth is as follows; The SiO_2/Si substrate was processed to form the corrugated pattern using the electron beam lithography and CF_4 plasma etching. The planed width and spacing of the corrugated pattern is 100nm and its depth is 40nm. After the formation of the corrugated pattern, 0.5nm thick Co catalyst is formed at the end of the corrugated pattern by the photolithography. Then the sample was set in the thermal CVD to grow the CNT at 800C. The CNTs which started to grow from the catalyst are attracted to the upper edge of the corrugated pattern and follow the direction of the corrugated pattern. So, the direction of the CNT growth can be controlled at our will only by forming the corrugated pattern on SiO_2/Si substrate.

The direction controlled growth of CNT on the corrugated pattern was confirmed by SEM observation. The CNT grew more than 7mm straightforward along with the corrugated pattern. Furthermore, it becomes clear that the CNT follows not on the bottom edge but at the upper edge of the corrugated pattern by the SEM observation from the tilted angle. In order to clarify the reason why CNT is attracted to the upper edge of the corrugated pattern, the Casimir force, which is a kind of van der Waals force, along with the cross section of the corrugated pattern was calculated. In the calculated results, the density of the Casimir force shows the highest peaks near the upper edges of the corrugated pattern. Because of these highest peaks of the Casimir force density, it becomes clear that the carbon nanotube is attracted to the upper edge of the corrugated pattern and grow following the direction of the pattern.

By applying this technology, FET with the direction controlled CNT channel was fabricated and its electrical property was examined. From the SEM observation, it was confirmed 8 CNTs were bridged between the source and drain electrodes. The dependence of the drain current on the gate bias at room temperature was examined, and the drain current reached as high as 2.5mA at V_g = -5V, which is about ten times higher than the conventional CNT FET. This is because a number of CNTs bridged between the source and drain electrodes can work as channels of FET.

5:40pm **NS-WeA12 Field Emission Properties of Wall-Number-Selected Carbon Nanotube Arrays**, ***D.H. Lee***, *S.O. Kim, W.J. Lee*, KAIST, Republic of Korea

The wall-number-selective growth of vertical carbon nanotube (CNT) arrays is achieved by the combination of block copolymer lithography and plasma enhanced chemical vapor deposition of CNTs, and the field emission properties were measured as a function of wall-number, length, density and doping concentration of CNT arrays. Block copolymer lithography is an attractive nanopatterning method for generating a uniform catalyst particle arrays for carbon nanotube growth. In this work, highly uniform nanopatterned iron catalyst arrays were prepared by tilted evaporation through block copolymer nanotemplates, and the sub-nanometer-scale tunability of catalyst particles enabled the excellent controllability of the wall-number and density of the CNT arrays. Moreover, the use of ammonia in the growth of CNT arrays ensured that the CNTs were nitrogen doped, and the doping concentration of nitrogen can be adjusted by controlling the flow rate of ammonia gas. Substitution of a carbon in a CNT wall with a more electron-rich nitrogen atom provided additional electrons and enhanced the conductivity of the nanotubes. With the excellent controllability of CNT arrays, we investigated the field emission properties of the grown CNT arrays. Wall-number, length, density and the doping concentration of CNT arrays were changed independently to investigate their effect on the field emission properties. Therefore, superior field emission performance of CNT arrays was acquired by controlling the physical and chemical parameters of CNT arrays.

Plasma Science and Technology
Room: A1 - Session PS1-WeA

Plasma Modeling
Moderator: M. Shen, AMAT

2:00pm **PS1-WeA1 Plasma Prize Lecture - Modeling and Simulation of Microplasma Discharges**, ***D.J. Economou****, University of Houston **INVITED**

High pressure (100s of torr) microplasma (length scale 100s of microns) discharges have potential applications as chemical microreactors, sensors, microelectromechanical systems (MEMS), and excimer radiation sources. Modeling and simulation of these systems, combined with plasma diagnostics, can provide critical information on fundamental discharge characteristics, and help extend the window of stable microdischarge operation. This talk will review the modeling and simulation methodologies used for microplasmas, with special emphasis on the coupling between plasma and neutral gas flows. The effect of operating conditions on gas temperature and in turn on discharge characteristics will be discussed in detail. Similarities and differences in modeling and operating characteristics between microdischarges and macroscopic discharges will be detailed. Simulation predictions will be discussed in light of spatially resolved plasma diagnostics used to measure important microdischarge properties (electron density and temperature, gas temperature, excited state densities, electric fields, etc.).

Work supported by the Department of Energy and the National Science Foundation

2:40pm **PS1-WeA3 Feature Scale Modeling of High Aspect Ratio Dielectric Etch**, ***P.J. Stout***, *J.A. Kenney, S. Rauf*, Applied Materials

Discussed will be results of three dimensional feature scale modeling of high aspect ratio (HAR) dielectric etching. The feature model is coupled to a reactor model which supplies specie flux values and angle and energy distribution functions to the feature model. The feature model has been used to study the mechanisms which contribute to the HAR etched profile. The mechanisms in the model include etchant transport to the surface, specular and diffusive reflection within the feature, adsorption, surface diffusion, energy loss, deposition, and etching. Typical requirements for HAR dielectric etch include reduction of profile bow, no off-axis profiles (i.e twisting, tilting), large bottom cd's, and no bottom profile distortion or rotation. Mechanisms contributing to off-axis etch profiles and bottom distortion will be discussed including mask shape, polymer deposition, etch by products, off-axis ion incidence, and yield curves. The effect of source power, bias power, and frequency mixing on the etched profile will also be explored. The shape of the mask at the opening controls the amount and direction of etchants entering the feature. Thus, the shape and evolution of the feature mask opening plays a large role in the evolution of the etched profile. For instance, a more angled mask increases the bow of the etched profile for a fixed process. Mask shape influences how polymer builds up at the opening and how the hard mask facets at the opening. Polymer buildup at the feature lip alters the path of striking ion incident near the feature opening. Facets forming at the feature opening also steer a portion of incoming ion flux from their largely wafer normal trajectory inside the feature. So the evolution of the mask shape over the course of the etch influences the ion trajectories and neutral shadowing to the etch front changing the character of the etched dielectric profile as the etch process proceeds.

3:00pm **PS1-WeA4 Feature Profile Evolution: From Plasma Etching and Deposition to Surface Roughness Formation and its Propagation**, *J. Hoang*, ***J. Chang***, University of California, Los Angeles

The limit of current integrated circuit device sizes is defined by state of the art processing technology, including the interplay between photolithography and pattern transfer by plasma etching. These two processes have a convoluted relation among complex surface kinetics, physical dependencies, and gas phase flux distributions that define the evolution of surface features. In this work, a model is developed to investigate the feature profile evolution during deposition and etching with a focus on roughness formation and its propagation. Surface kinetics is based on a translated mixed layer model (TMLM) develop by Kwon et. al.[1] and is implemented in a 3D Monte Carlo simulation domain. Ion incident angle dependence and an elliptical energy deposition model were used to capture the effects of surface morphology on the profile evolution under the bombardment of energetic and directional ions. Species fluxes are determined from experiments or through a reactor scale model.[2] Specifically, we examine chlorine-based plasma etching and how passivating species affect roughness formation through modification of the local surface composition. A translated mixed layer kinetics model is fitted to chlorine plasma beam etching experiments on silicon dioxide, and the reaction parameters are extracted to determine the relative etch yield on partially oxidized surfaces. Atomic force microscopy measurements of chlorine plasma etched Si with varying amounts of O_2 addition in the feed gas are compared to the simulated roughness and show qualitatively good agreement. For ionized deposition, we investigate the effects of roughness and geometry on the deposition conformality. The directionality of the ions along with the extent of physical sputtering is investigated and extracted from experimental SEM images. These parameters are then incorporated into the feature scale model, where the effects of propagation and geometry are investigated and show reasonable agreement with the observed SEM images.

[1] Kwon et al. Journal of Vacuum Science and Technology A. 24(5) 2006

[2] Hsu et al. Journal of Vacuum Science and Technology B. 26 (6) 2008

4:00pm **PS1-WeA7 Three-Dimensional Modeling of Ion Angular and Energy Distributions in Capacitively Coupled Plasmas**, ***J.A. Kenney***, *P.J. Stout, S. Rauf, K. Collins*, Applied Materials

As high aspect ratio (HAR) etch requirements continue to grow more stringent, it has become increasingly important to understand the influence of reactor design and process conditions on three closely intertwined areas: plasma uniformity; fluxes, energies, and angular distributions of species exiting the plasma and impinging on the wafer; and profile evolution of the HAR features. Due to the complexities and uncertainties involved in experimental analysis of these topics, many modeling efforts have been directed at each. Here, we investigate the unique aspects arising when each realm is considered fully in three dimensions in the context of a capacitively coupled plasma (CCP) reactor, with an emphasis on ion angular and energy distribution functions (IAEDFs).

Our efforts include a three-dimensional fluid plasma model, a Monte Carlo-based particle simulation for charged species, and a three-dimensional Monte Carlo-based feature profile evolution tool. The plasma model provides spatially and temporally-resolved species densities, species fluxes, and electric fields. The particle simulation uses that information in turn to generate ions in the bulk plasma and track them as they are influenced by

---

* 2008 Plasma Prize Winner

the time-varying electric fields as well as collisions with other species. The energy and three-dimensional angle for ions striking the wafer are recorded and binned as appropriate. The feature profile evolution tool uses this data along with the species fluxes from the plasma model as inputs and includes a variety of physics and chemistry, including ion-enhanced etching, ion sputtering, ion scattering, etch product desorption, and the formation of surface layers.

In this work, we demonstrate the influences of externally applied magnetic fields and azimuthally asymmetric reactor components in CCP systems on the resulting IAEDFs. To isolate the impact of these features, we consider simple etch-relevant feed gas mixtures (Ar, Ar/CF_4, Ar/O_2) and single (162 MHz) and dual frequency (2/60 MHz) configurations. We analyze both the differences between the IAEDFs generated with and without these features as well as differences found between locations within a single wafer. We then examine the linkage between these differences and the results from the feature profile evolution tool.

4:20pm **PS1-WeA8 A Global (Volume Averaged) Model of the Chlorine Discharge**, *E.G. Thorsteinsson*, ***J.T. Gudmundsson***, University of Iceland

A steady state global (volume averaged) model is developed for the chlorine discharge using a revised reaction set [1]. Various calculated plasma parameters are compared to measurements found in the literature, showing a good overall agreement. The reaction rates for the various reactions are evaluated in the pressure range 1 - 100 mTorr. In particular we explore the dissociation process as well as the creation and destruction of the negative ions Cl^-. The discharge is highly dissociated throughout the pressure range explored, 1 - 100 mTorr, even when the absorbed power is low. The mechanism for Cl creation is complex, although electron impact dissociation dominates with roughly 50 - 60 % contribution. Dissociative electron attachment is also of importance and mutual neutralization is an important contributor to the production of Cl atoms at higher pressure. The electronegativity increases rapidly with decreasing dissociation fraction since the Cl- ions are created entirely by dissociative electron attachment, predominantly from $Cl_2(v=0)$, but also up to 14 % from $Cl_2(v>0)$ at 100 mTorr. The negative ion Cl^- is lost almost entirely through mutual neutralization with Cl_2^+ at high pressure while Cl^+ has a significant contribution at low pressure. Furthermore, the dilution by argon was explored. Dilution by argon decreases the electronegativity but increases the electron temperature, dissociation fraction and the fractional density of Cl^+ ions significantly.

[1] E. G. Thorsteinsson and J. T. Gudmundsson, A global (volume averaged) model of the chlorine discharge, Plasma Sources Sci. Technol., submitted 2009

4:40pm **PS1-WeA9 Characterization of Very High Frequency Capacitively Coupled Plasmas**, ***K. Bera***, *L. Dorf, S. Rauf, K. Collins*, Applied Materials, Inc.

As semiconductor technology progresses to the 22 nm node, it is becoming increasingly important to fundamentally understand plasma etching processes and apply this understanding to development and improvement of plasma etch equipment. Capacitively coupled plasmas (CCP) have been widely used for dielectric plasma etching. The general trend in recent years has been towards the use of multi-frequency CCPs which include rf sources in the very high frequency (VHF) regime. We characterize one such system in this paper using two/three-dimensional (2/3D) plasma modeling. Modeling results are validated using experimental data for different operating conditions. Plasma simulations have been performed using our in-house 2/3D fluid plasma model. To account for electromagnetic effects at VHF, this 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. Model validation is performed using radially-resolved electron and ion densities and electron temperature measured with single and double Langmuir probes [1]. Ion density profiles obtained with both probes are generally similar over the range of conditions investigated. Plasma simulations were performed for a wide range of operating conditions [gas pressure (50 – 150 mT), rf power (100 – 1000 W), gases (Ar, O_2, CF_4)] at 60 and 162 MHz with and without a spatially inhomogeneous magnetic field. In agreement with experimental data, we observe that plasma density increases with pressure in Ar while the bulk plasma electron temperature is almost invariant. Plasma density is substantially higher at the higher frequency of 162 MHz. Plasma density is lower in electronegative gases than Ar under identical conditions. Plasma profile changes substantially with application of magnetic field, and the effect of magnetic field is weaker at higher pressures. While electromagnetic effects are strong at 162 MHz, reactor design determines the relative importance of electromagnetic vs. electrostatic effects at 60 MHz.

[1] L. Dorf et al., 2009 AVS Symposium.

5:20pm **PS1-WeA11 Investigation of Standing Wave Formation in the Large Area Capacitively Coupled RF Driven Processing Plasma Source**, ***S.H. Lee***, *M.S. Choi, G.H. Kim*, Seoul National University, Republic of Korea

Large area capacitively coupled plasma (CCP) sources are widely used in etch and deposition processes for the fabrication of flat panel display and solar cells. In general, the plasma density may increase with increasing frequency and it may improve the process rate. However the wavelength reduces with increasing frequency and the field variation on the substrate becomes serious due to the formation of standing wave pattern on the electrode. It causes the difficulty to control the process uniformity for the large process area. Many experimental investigations have been carried out for intermediate size plasma source as 1m x 1m and the wave patterns are observed. However, in practice, the reactor size becomes more than 2m x 2m with 13.56 MHz or higher RF frequency. Thus the standing wave effects are issued on the development of large area plasma process. The mechanism of standing wave formation and measurement are the theme of this study. Transmission line and wave models were developed to investigate the standing wave effect, skin effect, and telegraph effect, which have been reported separately. Here the new 1 D analytic model is introduced to describe the formation of standing wave on the reactor of 1.4m x 1.6m with applying 60 MHz, which consists of the transmission line model adapted to analysis of wave pattern from the matcher to the electrode and the wave propagation model for the formation of standing wave between sheath boundary and conducting electrode. Strategically, the wave conditions obtained from the transmission line model are adapted to the boundary values for the wave model. From this model, it reveals that the standing wave formation is related to the structure between the electrode and matching units as well as plasma property. Experimentally, the amplitude of plasma potential fluctuation was monitored from Langmuir probe measurement, being compared to the prediction of wave pattern from the model. It shows fairly good agreement between the model and the measurement. As expected, with increasing the plasma density, the wavelength becomes decreased due to shortening of the sheath thickness. Further results will be presented.

Plasma Science and Technology
Room: B2 - Session PS2+MN-WeA

High Aspect Ratio and Deep Etching for 3D Integration and Memory
Moderator: S. Hamaguchi, Osaka University, Japan

2:00pm **PS2+MN-WeA1 Advanced DRIE Via Etching**, ***F. Gao***, *D. James, K. Kolari, J. Kiihamäki*, VTT Technical Research Centre of Finland, *M. Muggeridge*, Aviza Technology, Inc.

We present 3 different types of interconnection vias fabricated by deep reactive ion etching (DRIE) on silicon substrates. One type of vertical vias with 30μm diameter mask opening are etched through 400μm thick wafer by switched Bosch process, featured by very fast etch rate at about 6μm/min and over 12:1 aspect ratio. The other type of vertical vias are tested on smaller diameters ranging from 1-9μm and etched to 20-50μm deep. Those vias have the minimum undercut and smooth sidewalls achieved by non-switched etching. Another type of tapered vias with 75μm mask opening are etched isotropically in DRIE resulting in over 150μm deep vias with 70-80 degree tapering. Silicon etch selectivity against different mask materials are studied and compared for the vertical vias. Thick resist is thought to be better mask to minimize undercut and via top erosion by reflected ions. Tapered vias have the problem of sidewall roughness from the isotropic etch. Both plasma cleaning and argon annealing methods are tested to smooth the silicon sidewalls in the tapered vias.

2:20pm **PS2+MN-WeA2 The Generation and Removal of Heat during DRIE of High Aspect Ratio Structures in SOI with Buried Cavities**, ***J. Dekker***, *F. Gao, J. Kyynäräinen, J. Kiihamäki*, VTT Microelectronics Research Center of Finland

This work examines the accumulation of heat and resulting increase in local temperature and loss of selectivity which may occur when etching high aspect ratio structures in SOI wafers with buried cavities. It is shown that unlike high-load, high-rate etches treated elsewhere, in the case of HAR etches the heat is generated mainly by ion-bombardment. Due to the presence of a cavity beneath the structures being released, which typically include a mass suspended by springs, the heat may only be conducted laterally away from the released structures to the surrounding device layer. During the final stages of DRIE etch and overetch, the heat flow from suspended masses is therefore restricted to occur along the springs which attach the mass to the surrounding device layer. The limited heat conductance of long meander springs in particular is unable to remove the heat generated in suspended structures. As a result, the temperature of the suspended structures increases resulting in reduced fluorocarbon depositon upon them. That, in turn, results in a locally increased etch rate of the oxide mask on the suspended structures. The effects of releasable thermal anchors, which provide additional paths for heat conduction away from the suspended mass and therefore aid in the removal of heat, is also discussed.

2:40pm **PS2+MN-WeA3 Ion Trajectory Prediction at High-Aspect-Ratio Hole Etching by the Combination of On-Wafer Monitoring and Sheath Modeling**, ***H. Ohtake***, *S. Fukuda, B. Jinnai,* Tohoku University, Japan, *T. Tatsumi,* OKI Semiconductor Miyagi Co., Ltd., Japan, *S. Samukawa*, Tohoku University, Japan

The abnormal etching profiles, such as bowing, etch stop and twisting, have been reported at high-aspect-ratio hole etching. To avoid the failures, we have to predict the ion trajectory and etching profile precisely by analyzing the sheath area around the hole. In this presentation, we developed the ion-trajectory prediction system at high-aspect-ratio hole by combining the on-wafer monitoring technique and sheath modeling for explaining and predicting the etch stop and twisting. Since our developed on-wafer sensors provide the surface potential, the electron density/ temperature and side-wall resistance of the hole, we can simulate the distribution of electric field in the hole. This system revealed that the sidewall conductivity strongly affects the charge-up and ion trajectory in the high-aspect-ratio hole. It also predict the etch stop and twisting phenomena. Consequently, we believe this prediction system is an effective tool for developing the nano-scaled fabrication.

3:00pm **PS2+MN-WeA4 Enhancement Mechanism of Distortion and Twisting in Ultra High Aspect Ratio Dielectric Etching**, ***H. Mochiki***, Tokyo Electron AT Ltd., Japan, *K. Yatsuda,* Tokyo Electron Ltd., Japan, *S. Okamoto, F. Inoue*, Tokyo Electron AT Ltd., Japan

It is required to fabricate capacitors with aspect ratio of from 40:1 to 60:1 for DRAM at hp 3x nm and beyond generation, and etching such ultra high aspect cylindrical shapes without distortion and/or twisting is the most difficult challenge. Recently, it has been reported that distortion and twisting were caused by electron shading effects, electrical potential difference between the top and bottom of dielectric during plasma etching. In this paper, we report how distortion and twisting are enhanced, and how they can be minimized.

First of all, electron shading effects are results of electrostatic charge on the surface of etched dielectric material – silicon dioxide, and organic capacitor mask is negatively charged where silicon dioxide surface is positively charged. At these generations, DRAM devices are so largely scaled that their capacitors need to be fabricated very close to each other. Consequently, incident positively charged ions in a cylinder, accelerated by plasma sheath, receive repulsive force from not only the cylinder surface itself but also neighboring cylinder surfaces. We confirmed that grad of distortion and twisting changed by altering the layout of capacitors.

On the other hand, we found that distortion and twisting could also be generated from the very beginning of etching at the low aspect ratio portion by observing the top view of a cylinder every 100 nm-deep from the wafer surface. Moreover, we affirmed that distortion strongly correlated with capacitor etch mask profile when varying it on purpose by changing mask etch conditions. Thus, we clarified that another enhancement mechanism of distortion existed apart from electron shading effects.

Therefore, there are several enhancement mechanisms of distortion and twisting, and it is necessary to address each solution. We divided the enhancement mechanisms of distortion and twisting into two modes, which are generated at low and high aspect ratio, and examined their solutions from the etching point of view, respectively. We conclude that the optimization of capacitor etch mask profile was the most effective solution at the low aspect ratio mode, and higher dissociation plasma with relatively higher plasma density and superimposed DC on CCP (capacitively coupled plasma) improved distortion and twisting at the high aspect ratio mode.

4:00pm **PS2+MN-WeA7 High Rate Deep Si Etching for TSV Applications**, ***I. Sakai***, *N. Sakurai, T. Ohiwa*, Toshiba Corporation, Japan **INVITED**

Si etch process for etching deep and high-aspect ratio structures has been studied intensely for applications such as DRAM trench capacitors and MEMS devices. Recently, there is focus on Si etching for TSV (through Si via) applications for 3-D (three-dimensional) LSIs. Dimensions of the TSVs which are being investigated today vary widely, depending on its application and integration scheme. For example, TSV for 3-D packaging of logic devices may be sub-micron to a few microns in diameter and about 10 microns deep. On the other hand, TSVs used in stacking memory devices, the via diameter and depth would be several tens of microns, and, package for CMOS image sensors using TSVs may have via diameters and depths up to 100 microns.

For TSVs up to 10 microns in depth, the conventional Si deep trench etch process for DRAMs can be easily adapted to etching TSVs because of its similar dimensions. The typical etch rate is several microns per minute. On the contrary, etching of very deep holes of depths on the order of tens of microns and up to 100 microns is not within the experience of conventional front-end LSI fabrication processes. In this case, consequently, an extremely high Si etch rate becomes mandatory because of cost issues, especially for TSV applications which require via holes more than 20 microns deep.

To fulfill this requirement for TSV applications, the Si etch process was investigated focusing on the Si etch rate. First, a large via size of 40 microns was studied, and an etch rate of more than 50 µm/min was realized. It was found that the Si etch rate depended on fluorine radical density, so, high rate was obtained by creating a high fluorine radical density condition by using a high pressure condition of 350 mTorr, with a capacitively-coupled plasma (CCP) reactor with a Dipole-Ring Magnet (DRM) and SF_6 gas chemistry. Furthermore, the etch process for smaller holes of 8 microns was studied to realize high etch rates also. The etch process was modified to obtain a straight etch profile, then, via holes were etched to a depth of 60 microns at an etch rate of 24 µm/min.

High rate deep Si etching is realized for TSV application for holes more than 20 microns deep, using CCP RIE with SF_6–based gas chemistry.

4:40pm **PS2+MN-WeA9 Infinitely High Etch Selectivity and Variation of Line Edge Roughness during Etching of Hard-Mask Layer with Patterned Extreme Ultra-Violet**, ***B.S. Kwon***, *J.S. Kim, C.R. Jung, J.S. Park, W. Heo, N.-E. Lee,* Sungkyunkwan University, Korea, *S.K. Lee*, Hynix Semiconductor, Republic of Korea

In the nano-scale Si processing, patterning processes based on multilevel resist structures becoming more critical due to continuously decreasing resist thickness and feature size. In particular, highly selective etching of the first dielectric layer with resist patterns and control of critical dimension (CD) and ling edge roughness (LER) are of great importance. In this work, process window for the infinitely high etch selectivity of silicon oxynitride (SiON) layers to EUV resist and variation of LER of extreme ultra-violet (EUV) resist was investigated during etching of SiON/EUV resist in a $CH_2F_2/N_2/Ar$ and $CH_2F_2/N_2/O_2/Ar$ dual-frequency superimposed capacitive coupled plasma (DFS-CCP) by varying the process parameters, such as the CH_2F_2 and N_2 flow ratio, low-frequency source power (P_{LF}) and O_2 flow rate. It was found that the CH_2F_2/N_2 flow ratio was found to play a critical role in determining the process window for infinite SiON/EUV resist etch selectivity, due to the differences in change of the degree of polymerization on SiON and EUV resist. Control of N_2 flow ratio gave the possibility of obtaining the infinitely high etch selectivity by keeping the steady-state hydrofluorocarbon layer thickness thin on the SiON surface due to effective formation of HCN etch by-products and, in turn, in continuous SiON etching, while the hydrofluorocarbon layer is deposited on the EUV resist surface. On the other hand, CD size and LER tend to increase with increasing CH_2F_2/N_2 flow ratio.

Surface Science
Room: M - Session SS1-WeA

Water/Surface Interactions & Environmental Chemistry II
Moderator: V. Grassian, University of Iowa

2:00pm **SS1-WeA1 Towards Understanding the Formation of Water in the Interstellar Medium**, ***V.L. Frankland***, *M.P. Collings, M.R.S. McCoustra*, Heriot-Watt University, UK

Exposed to the harsh radiation fields of interstellar space, few molecules can escape photodestruction. However, the vast clouds of gas and dust that accumulate in the gulfs of space between the stars (known as the interstellar medium) have been observed to contain more than 120 different molecular species[1]. The low temperature (10-100 K) and pressure (10^{-14} mbar) conditions within the interstellar medium limit the range of viable gas-phase reactions resulting in the gas-phase chemistry alone being insufficient to explain the observed abundances of some key chemical species (for example, H_2 and H_2O). Dust grains provide a surface on which adsorbed species can react[2] and hence an alternative pathway to key interstellar molecules. Indeed, this has been proven for the efficient formation of H_2 both experimentally[3-6] and computationally[7-9].

Surface chemistry within an ultrahigh vacuum chamber is being used to explore the surface irradiation reactions of O on a range of astrophysically relevant surfaces using atomic beam methods. In these experiments, the products are identified using temperature programmed desorption. The results of the experiments are interpreted using kinetic analysis of a simple surface mechanism. Analogous experiments will be conducted using an atomic H beam. The ultimate aim of this research will be to combine the two beams to study *in situ* H_2O formation on a grain surface.

References

1) from “129 reported interstellar and circumstellar molecules” http://www.cv.nrao.edu/%7Eawootten/allmols.html [http://www.cv.nrao.edu/~awootten/allmols.html] (assessed 7th May 2009)

2) R. Gould, E.Salpeter, *Astrophys. J.*, 1963, **138**, 393

3) G. Vidali, J. Roser, G. Manico, V. Pirronello, *Adv. Spa. Res.*, 2004, **33**, 6

4) L. Hornekaer, A. Baurichter, V. Petrunin, A. Luntz, B. Kay, A. Al-Halabi, *J. Chem. Phys.*, 2005, **122**, 124701

5) F. Dulieu, L. Amiaud, S. Baouche, A. Momeni, J. Fillion, J. Lemaire, *Chem. Phys. Lett.*, 2005, **404**, 187

6) J. Perry, J. Gingell, K. Newson, J. To, J. Watanabe, S. Price, *Meas. Sci. Technol.*, 2002, **13**, 1414

7) O. Biham, A. Lipshtat, *Phys. Rev. E*, 2002, **66**, 56103

8) N. Katz, I. Furman, O. Biham, V. Pirronello, G. Vidali, *Astrophys. J.*, 1999, **522**, 305

9) H. Cuppen, E. Herbst, *Mon. Not. Roy. Astron. Soc.*, 2005, **361**, 565

2:20pm **SS1-WeA2 Photon- and Electron-stimulated Desorption from Laboratory Models of Interstellar Ice Grains**

J.D. Thrower, A.G.M. Abdulgalil, M.P. Collings, ***M.R.S. McCoustra***, Heriot-Watt University, UK, *F.J.M. Rutten*, Keele University, UK

Dense molecular clouds, in our own and other galaxies throughout the Universe, are the seats of evolution in the present day Universe. New stars and their planetary systems are born in such environments from the chemically rich soup of gas and icy dust from which these environments are made. In the last decade or so, astronomers have turned to the surface science community to help explain the role played by physical and chemical processes in coupling of the gas and solid (dust grain) phases in these crucially important regions of space.

We have recently been investigating one key aspect of that gas-grain interaction; the role played by non-thermal (photon- and low energy electron-driven) processes in returning components of the icy grain mantle to the gaseous interstellar medium. Ultrathin layers of predominantly water (H_2O) ice grow reactively on dust grains; such layers can accumulate adsorbed volatiles such as carbon monoxide (CO) from the gaseous interstellar medium and are observed with sufficient ease in the infrared to be mapped. Indeed such icy mixtures are firmly believed to be the home of chemical evolution in these dense environments as the simple ices (H_2O, CO, NH_3 *etc.*) are converted by a combination of thermal and non-thermal processes into more complex species (*e.g.* CO_2, CH_3OH, CH_3NH_2 *etc.*). Further processing of these complex icy mixtures may lead to the formation of prototypical molecules which may, following exogenous delivery to a nascent planet, provide the raw materials for biological evolution. However such a drive towards increasing chemical complexity takes time; time in which competition from non-thermal desorption processes may in fact remove the icy mantle from its substrate exposing the fragile molecular contents to the harsher environment of the gaseous interstellar medium. We describe preliminary studies of both photon- and low energy electron-driven desorption from a model interstellar ice deposited on model grain surfaces under UHV conditions. We will report on the rates of desorption mediated by photon- and electron-stimulated interactions and, where known, outline the dynamical consequences of such desorption.

2:40pm **SS1-WeA3 Structure-Property Relationships of Water Interfaces 200° Beyond the Boiling Point**

S. Putnam, *L. Gschwender*, Thermal and Materials Sciences Branch - WPAFB

In cooling technologies that utilize the latent heat of vaporization (e.g. pool boiling and spray cooling), knowledge of the critical heat flux is “critical.” Beyond the critical heat flux, a continuous vapor layer forms at the solid-liquid interface that impedes heat transfer. The formation of this chaotic, thermally-resistive vapor layer” is well known. However, our recent research has demonstrated that a new, unique, and stable water interface is formed beyond the critical heat flux for surface temperatures 100+ degrees above the boiling point. At this point, film boiling stops, forming a smooth, highly light reflective, high surface energy water interface that further impedes heat transfer. We present our efforts in correlating the thermal, mechanical, and structural properties of this unique water interface using high-speed imaging, Raman spectroscopy, and numerical modeling. Critical heat flux data as a function of vapor pressure is also presented for water boiling on patterned surfaces of carbon nanotubes and nanowire whisker arrays.

3:00pm **SS1-WeA4 Proton and Water Self-diffusion in Thin Layers of Amorphous Solid Ice Studied by FTIR and DFT Calculations**

P.E. Uvdal, *J.E. Blomquist*, Lund University, Sweden

We have studied the H/D exchange in both two- and three-dimensional thin layers of 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 sandwiched layers at 84 K. By careful pretreatment of the surface we can control the proton diffusion, thereby allowing for a separation and a characterization of the two diffusion processes. The role of the Grotthuss mechanism for the observed H/D exchange will be discussed. Using infrared vibrational spectroscopy we can monitor the isotopic mix of water molecules both at the ice surface as well as in the solid ice. A detailed understanding of the vibrational data is obtained with the aid of DFT cluster calculations.

4:00pm **SS1-WeA7 Surface Science Studies of Environmentally Relevant Chemistry on Some Metal Sulfide and Oxide Minerals**

D.R. Strongin, Temple University **INVITED**

Studies are presented that investigated environmentally relevant chemistry on pyrite (FeS_2), birnessite (MnO_2), and nanocrystalline ferrihydrite. Photoelectron spectroscopy, in situ atomic force microscopy, and in situ infrared spectroscopy studies will be presented that address the oxidation of pyrite, arsenite adsorption on birnessite, and carbonate formation of ferrihydrite. Selected results from these studies will bring forward important issues related to the understanding of complex environmental chemistry occurring on mineral surfaces. In the arsenite/birnessite circumstance, for example, batch reaction measurements determined the extent of the conversion of the arsenite to arsenate and the amount of Mn(II) formed during this reductive dissolution process. Atomic force microscopy (AFM) investigated morphology changes during the reactions associated with birnessite as well as the nature of any precipitate phases by using phase imaging. The microscopy was complemented by X-ray photoelectron spectroscopy (XPS) that was able to determine the relative distribution of Mn(IV), Mn(III) and Mn(II) after reaction with As(III). Attenuated total reflection Fourier transform infrared spectroscopy (ATR-FTIR) was also used to determine the nature of the arsenic-species on the Mn oxide and oxyhydroxide surfaces.

4:40pm **SS1-WeA9 Water Growth on a Hydrophobic Substrate: Observation of a Metastable, Two-Layer Crystalline Ice on Graphene**

G.A. Kimmel, *J. Matthiesen*, Pacific Northwest National Laboratory, *M. Baer*, Ruhr-Universität Bochum, Germany, *C. Mundy, N.G. Petrik, R.S. Smith, Z. Dohnálek, B. Kay*, Pacific Northwest National Laboratory

The structure of water at interfaces is crucial for processes ranging from photocatalysis to protein folding. Here, we investigate the structure and lattice dynamics of two-layer crystalline ice films grown on a hydrophobic substrate – graphene on Pt(111) – with low energy electron diffraction, reflection-absorption infrared spectroscopy, rare-gas adsorption/desorption, and *ab-initio* molecular dynamics. Unlike hexagonal ice, which consists of stacks of *puckered* hexagonal “bilayers”, this new ice polymorph consists of two *flat* hexagonal sheets of water molecules in which the hexagons in each sheet are stacked directly on top of each other. Such two-layer ices have been predicted for water confined between hydrophobic slits, but not previously observed. Our results show that the two-layer ice forms even at zero pressure at a single hydrophobic interface by maximizing the number of hydrogen bonds at the expense of adopting a non-tetrahedral geometry with weakened bonds.

5:00pm **SS1-WeA10 $SrTiO_3(001)$ Surface Structure Stabilization Via Water Mediation**

A.E. Becerra-Toledo, *D.M. Kienzle, L.D. Marks*, Northwestern University

Strontium titanate, $SrTiO_3$, has been largely studied as the quintessential model system for perovskite oxides. In the field of surface science, the presence of multiple cation valence states has allowed for insights into the stabilization mechanisms in mixed-metal oxides. Multiple $SrTiO_3$ surface structures have been conclusively described at the atomic scale, which lets us go beyond bulk-like caricature descriptions of oxide surfaces. In turn, this allows for a more realistic study of the interaction of oxide surfaces with foreign species such as water, whose ubiquity makes such analysis inescapable.

Density functional theory (DFT) calculations were performed to study the surface energetics of several observed and theoretical $SrTiO_3(001)$ surface reconstructions, both dry and with chemisorbed water. A repeated slab configuration was used to model all surface structures, which include not only bulk-like truncations, but also the 2x1, c(4x2), $(\sqrt{13}x\sqrt{13})R33.7^\circ$ reconstructions, as well as the theoretically predicted low-energy $(\sqrt{2}x\sqrt{2})R45^\circ$ structure. The use of an augmented plane wave plus local orbital (APW+lo) basis, coupled to the full-electron potential implementation, accurately reflects the character of single-particle wavefunctions. The TPSSh hybrid meta-GGA exchange-correlation functional [Tao et al., PRL 91,146401 (2003)] was employed, which allows for an improved treatment of strongly correlated systems. Both the molecular and dissociative water adsorption modalities were taken into account.

Our analysis suggests that water mediation is responsible for the fact that the thermodynamically favorable $(\sqrt{2}x\sqrt{2})R45^\circ$ structure [Warschkow et al., Surf.Sci. 573, 446 (2004)] has never been detected while other reconstructions of identical stoichiometry and significantly higher surface energy, such as the 2x1, have been readily observed. In the latter, the adsorption of water is much more favorable, which insinuates that the formation of the $(\sqrt{2}x\sqrt{2})R45^\circ$ reconstruction is kinetically limited if there is any exposure to water vapor. Several experimental results back up this observation.

5:20pm **SS1-WeA11 Water Adsorption on O(2x1)-Ru(0001)**, *S. Maier, I. Stass,* ***M. Salmeron***, Lawrence Berkeley National Laboratory

We studied the adsorption of water on the O(2x1) -Ru(0001) surface at submonolayer coverage by low temperature scanning tunneling microscopy. We found that water reconstructs the oxygen layer from a linear configuration to a honeycomb structure with the water molecules incorporated inside, confirming a model previously proposed by Gladys et al. based on XPS measurements [1]. In addition, we found that water monomers inside the oxygen hexagons can rotate through interaction with the tip, while dimers are more stable.

[1] M.J. Gladys et al. PRB 78, 035409 (2008).

5:40pm **SS1-WeA12 Structure and Dynamics of Liquid Water on Surfaces from Ab Initio Molecular Dynamics: Graphene/Water and Alumina/Water**, ***P. Huang***, *E. Schwegler*, Lawrence Livermore National Laboratory

Many important surface phenomena occur under aqueous conditions, where water plays a significant but poorly understood role in interfacial structure and reactivity. Atomic-scale information at solid/water interfaces is notoriously difficult to unravel, and thus simulations are an essential complement to experimental efforts. To date, such simulations typically rely on simple, empirical models for interatomic interactions. However, there is a great deal of ambiguity in the parameterization of these potentials; often they are fitted to bulk properties, and the transferability to complex interfacial systems is unclear. Here, we report atomic-scale simulations of solid/water interfaces via ab initio molecular dynamics, where interatomic interactions are derived on-the-fly from density functional theory. Unlike empirical models, this approach is generally applicable to both bulk and interfacial environments, without input from experiment. Two prototype examples are considered: graphene/water as a model hydrophobic surface, and alumina/water as a model oxide surface. In both cases, a bulk-like liquid water layer at ambient conditions is explicitly included. We examine interfacial structure and dynamics, relate these to spectroscopic observables (infrared spectroscopy, nuclear magnetic resonance). Comparison to predictions from common empirical potentials is given in order to gain insight into when such models fail, and how they can be improved.

Surface Science
Room: N - Session SS2-WeA

Surface Physics, Single Particle Imaging
Moderator: M. Trenary, University of Illinois at Chicago

2:00pm **SS2-WeA1 Dynamics of Alkali Metals Adsorbed on Cu(111) at Low Density using High Resolution ^{3}He Spin-Echo Spectroscopy**, ***D.J. Ward***, *A.P. Jardine, H.J. Hedgeland, W. Allison, J. Ellis*, University of Cambridge, UK

Alkali atoms at surfaces show unexpected behaviour arising from the strong interadsorbate forces and coupling of electronic and nuclear motion [2,3]. In the present work we present new results giving additional insight into both the dynamics and the scattering.

High resolution quasielastic helium atom scattering (QHAS) experiments provide a unique tool to study adsorbate dynamics[1] since3He spin-echo measurements give the surface correlation in time through the intermediate scattering function (ISF), I(ΔK,t). The functional form of the ISF has a well defined analytic form for simple systems, however for real systems the form is typically complex and challenging to predict. For example the shape of the ISF can take a multifunctional form due to summation effects from multiple species or clusters moving with the same or different modes, and a convolution effect from differences in the local appearance of the potential energy landscape to the adsorbate for the length scale under study.

Previous investigations of the diffusion of alkali metals on metal surfaces have revealed unexpected phenomena. For sodium on Cu(100), a 'new' mode of aperiodic motion, perpendicular to the surface, was discovered[2]. For caesium, the observed dynamics on the same surface were found to be qualitatively different to sodium[3], indicating a critical balance of adsorbate-substrate and adsorbate-adsorbate interactions, determining the behaviour for each adsorbate.

In this work we present detailed helium-3 spin-echo QHAS measurements of the dynamics of sodium adsorbed on Cu(111) at low to moderate coverages. We observe a QHAS broadening with the presence of a complex lineshape which shows a momentum transfer variation. The functional form is compared with theoretical models[4] for different potential energy landscapes. The variation of the QHAS broadening with temperature and momentum transfer are studied to access information on the dynamic phenomena on the Cu(111) surface, exploring in particular the generality of perpendicular motion, and changes in the adsorbate-substrate/adsorbate-adsorbate force balance.

[1] A.P. Jardine, S. Dworski, P. Fouquet, G. Alexandrowicz, D. J. Riley, G. Y. H. Lee, J. Ellis, W. Allison, Science 304, 1790 (2004).

[2] G. Alexandrowicz, A. P Jardine, H. Hedgeland, W. Allison, J. Ellis, *Phys. Rev. Lett 97, 156103 (*2006)

[3] A P Jardine, G Alexandrowicz, H Hedgeland, R D Diehl , W Allison and J Ellis, J. Phys.: Cond. Matter 19 305010 (2007)

[4] R. Martinez-Casado, J.L. Vega, A.S Sanz, S. Miret-Artes, J. Chem. Phys.126,194711-5 (2007)

2:20pm **SS2-WeA2 MORTON S. TRAUM AWARD FINALIST: Direct Observation of Hydrogen-Bond Exchange within a Single Water Dimer**, ***T. Kumagai****, *M. Kaizu, H. Okuyama,* Kyoto University, Japan, *S. Hatta, T. Aruga,* Kyoto University, JST-CREST, Japan, *I. Hamada, Y. Morikawa*, Osaka University, Japan

The nature of the hydrogen bond is related to many physical, chemical and biological processes. The structure and dynamics of water dimers, which consist of hydrogen-bond donor and acceptor molecules, have been subjects of extensive research as a prototype of much more complex hydrogen-bonding systems. The water molecules in a free water dimer rearrange the hydrogen bond through quantum tunneling among equivalent structures [1]. Recently, we reported the visualization in real space of hydrogen-bond exchange process governed by quantum tunneling within a single water dimer adsorbed on a metal surface with a low-temperature scanning tunneling microscope (STM) [2].

The experiments were carried out in an ultrahigh vacuum chamber equipped with STM operating at 6 K. The Cu(110) was cleaned by repeated cycles of argon ion sputtering and annealing. The surface was exposed to H_2O or D_2O gases via a tube doser below 20 K. We conducted the experiments at very low coverages, where water molecules exist mainly as isolated monomers and dimers on the surface.

A water dimer is characterized by its bi-stable fluctuating image due to the interchange motion of the hydrogen-bond donor and acceptor molecules. The STM image of the dimer shows dramatic change upon substitution with heavy water. The interchange motion of $(D_2O)_2$ is much slower than that of $(H_2O)_2$. The interchange rate was determined to be $(6.0 \pm 0.6) \times 10\ s^{-1}$ for $(H_2O)_2$ and $1.0 \pm 0.1\ s^{-1}$ for $(D_2O)_2$ by monitoring the interchange events in real time. The large isotope effect (~60) suggests that the rate-limiting process involves quantum tunneling. In addition, DTF calculation revealed that the barrier of the interchange on Cu(110) is 0.24 eV. This cannot be overcome via mere thermal process at 6 K, which corroborates that the interchange proceeds through tunneling.

Furthermore, the interchange rate is enhanced upon excitation of the intermolecular mode that correlates with the reaction coordinate. While the interchange motion is intrinsic at low bias voltage, as indicated by negligible tip effect, it becomes tip assisted at voltages above 40 mV. The threshold voltage is determined to be 45 ± 1 (41 ± 1) mV for H_2O (D_2O) dimers. The barrier for the interchange (0.24 eV), however, much larger than the energy transferred from a tunneling electron (45 mV). Consequently, we propose that the interchange tunneling is assisted by vibrational assisted tunneling process.

---

* Morton S. Traum Award Finalist

[1] R. S. Fellers, C. Leforestier, L. B. Braly, M. G. Brown, and R. J. Saykally, Science 284, 945 (1999).

[2] T. Kumagai *et al. Phys. Rev. Lett.* 100, 166101 (2008).

2:40pm **SS2-WeA3 Single Molecule Assembly, Chirality and Catalysis**, ***C.E. Sykes***, Tufts University **INVITED**

Self-assembled monolayers (SAMs) offer many useful applications in the form of parallel nanostructure fabrication, lubricants for MEMS, corrosion protection and sensing. Thioethers are more resilient to oxidation than thiols and offer the potential for control over nanoscale assembly in two dimensions parallel to the surface. Low-temperature scanning tunneling microscopy (LT-STM) data demonstrates that thioethers form large, very well ordered domains with little or no defects that cover areas >1,000nm2. In contrast to alkane thiol assembly on the same surface, thioethers do not lift the Au {111} herringbone reconstruction. This feature facilitates defect-free thioether assembly which is not disrupted by etch-pit formation that alkane thiol SAMs suffer from. These data suggest the potential use of thioethers for a variety of self-assembly applications that require very perfect assembly and control over molecular spacing parallel to the surface.

Thioethers also constitute a simple, robust system with which molecular rotation can be actuated thermally, mechanically and electrically. By monitoring the rate of rotation as a function of tunneling electron energy (action spectroscopy) we have demonstrated that the rotors can be driven electrically via a mechanism that involves excitation of a C-H stretch. Forming ordered arrays of molecular rotors may provide entirely new approaches to signal processing, sensing, and energy modulation. For this application, an array of dibutyl sulfide rotors has been formed on a Ag/Cu{111} surface alloy. Molecular rotors can also act as standards by which scanning probe chirality can be measured and assigned. Such atomic-scale geometric data about the STM tip allows unambiguous chirality assignment on individual, isolated, molecule basis for the first time.

Palladium and its alloys play a central role in a wide variety of industrially important applications such as hydrogen reactions, separations, storage devices, and fuel cell components. The exact mechanisms by which many of these processes operate have yet to be discovered. LT-STM has been used to investigate the atomic-scale structure of Pd/Au and Pd/Cu bimetallics created by depositing Pd on both Au(111) and Cu(111) at a variety of surface temperatures. We demonstrate that individual Pd atoms in an inert Cu matrix are active for the dissociation of hydrogen and subsequent spillover onto Cu sites. Our results indicated that H spillover was facile on Pd/Cu at 400 K but that no H was found under the same H2 flux on a Pd/Au sample with identical atomic composition and geometry.

4:00pm **SS2-WeA7 Molecular Motion in Confinement**, *Z. Cheng, M. Luo, D. Sun,* ***L. Bartels***, University of California at Riverside

CO diffusion within a honeycomb network of anthraquinone molecules on a Cu(111) will be presented. The motion of the molecules is strongly affected by the confinement provided by the network. We observe the formation of a shell structure within pores, diffusion rates that strongly depend on the coverage and imperfections of the coverage (e.g. dislocation lines) that appear thermodynamically stable.

4:20pm **SS2-WeA8 Spatial Images of Different Vibronic Peaks at Single Molecule Level**, ***Q. Huan***, University of California, Irvine and Chinese Academy of Sciences, *H.J. Gao,* Chinese Academy of Sciences, *W. Ho*, University of California, Irvine

Spatial distributions of different vibronic peaks on single naphthalocyanine molecules adsorbed on an ultrathin aluminum oxide film are imaged by a scanning tunneling microscope in real space at low temperature. The spatial variations of electron-vibronic coupling in these images reveal the interplay between the molecular comformation, the vibrational modes and the molecular orbital structure, which are in accordance with spectra recorded at different locations over the molecule.

This work shows that vibronic imaging can provide rich information of electron-vibrational coupling at the single molecule level.

4:40pm **SS2-WeA9 Stepwise Control and Spectroscopic Manifestation of the Target-Selective Single Bond Dissociation and Formation**, ***Y.J. Jiang***, *W. Ho*, University of California, Irvine

We demonstrated here, adopting a thiol-based π-conjugated molecule (1,4-bis[4'-(acetylthio)styryl]benzene), the evolution of the molecular electronic structure with the stepwise abstraction of different functional groups and the attachment of single gold atoms to sulfur anchoring atoms by scanning tunneling microscope (STM). The electronic resonances of the resultants were measured by spatially resolved electronic spectroscopy at each reaction step. It was revealed that the target-selective bond dissociations were initiated by electron populations of the spatially localized and energetically separated electronic resonances. Combining the well-controlled single bond scission with the lateral manipulation by STM tip, the details of Au-S bond formation and the influence of Au-S interaction on the electronic structure of the molecular junction were investigated in the well-defined contact geometry.

5:00pm **SS2-WeA10 Surface Dynamics of Molecules in Single Internal (Vibrational and Rotational) States**, *V.L. Campbell, N. Chen,* ***A.L. Utz***, Tufts University

Beam-surface scattering studies of molecules prepared in a single internal quantum state provide a high level of control over the energetics and internal motion of the gas-phase reagent. Varying the identity of the laser-excited state permits a systematic survey of how vibrational excitation in the gas-phase reagent (bending or stretching excitation) impacts reactivity and reveals that both vibrational mode-selective and bond-selective chemistry is possible in a gas-surface reaction. Recently, we have begun to exploit the energetic control this approach offers to probe the dynamics of other energetic degrees of freedom. For example, state resolved reactivity measurements (S_0 vs. E_{trans}) of CH_4 dissociation on Ni(111) show that the shape of the sticking curve changes as a function of surface temperature. This change likely results from the modulation of the effective barrier to reaction along the translational energy coordinate as a function of surface atom position. Our experimental results are consistent with recent theoretical studies that point to an important role for surface atom motion in promoting dissociative chemisorption on Ni and Pt surfaces. The presentation will focus on our use of state-selected reagents to probe dynamics associated with other energetic degrees of freedom, such as surface atom motion. It will also describe advances in our experimental methods for acquiring these state-resolved data. These advances are transforming our ability to perform state-resolved measurements and will enable our extension of these methods to a much wider array of chemical systems.

5:20pm **SS2-WeA11 3-Dimensional Velocity Map Imaging from Surfaces: A New Technique for the Study of Photodesorption Dynamics**, *S.P. Koehler, Y. Ji,* University of California, Santa Barbara, ***D.J. Auerbach***, GRT Inc., *A.M. Wodtke*, University of California, Santa Barbara

The ion imaging technique and the improved velocity map imaging (VMI) technique [1] have been successfully applied to many gas-phase photo-dissociation and crossed-beam experiments over the last 20 years [2]. The VMI technique maps two dimensional product velocity distributions to an image on a position sensitive detector and thus allows the measurement of product flux as a function of velocity for all velocities simultaneously.

Experiments on photo-desorption from surfaces have so far not used this elegant technique. Such experiments have often relied on time-of-flight (TOF) techniques to gain dynamical information about the process under investigation [3].

Here we show how Time-of-Flight (TOF) measurements can be coupled to the VMI technique to yield 3-dimensional velocity distributions for desorption products of surface photochemistry. In one example, we applied this Three-Dimensional Surface Velocity Map Imaging (TDS-VMI) method to measure 193 nm photo-desorption of Br atoms from a KBr surface. Although this system has been studied in the past, the TDS-VMI technique reveals new features of the desorption dynamics. The velocity distributions indicate that at least two non-thermal mechanisms contribute to the photo-desorption dynamics. The TDS-VMI method also allows us to measure the yield of $Br(^2P_{3/2})$ and $Br(^2P_{1/2})$ over the full range of velocities that contribute to the photo-desorption process. The branching ratio $Br(^2P_{3/2})/Br(^2P_{1/2})$ is 24/1, a value that is quite different from that obtained previously.

Other examples will be discussed at the conference.

5:40pm **SS2-WeA12 Activated Quantum Diffusion of Hydrogen on Platinum(111)**, ***A.P. Jardine***, *E. Lee, G. Alexandrowicz, H.J. Hedgeland, W. Allison, J. Ellis*, University of Cambridge, UK

Hydrogen atoms are one of the few surface species that are of sufficiently low mass for quantum processes to dominate surface transport. Here, we present the first quasi-elastic helium atomscattering (QHAS) measurements that demonstrate clear quantum effects in adsorbate diffusion. We use helium-3 spin-echo to make dynamic equilibrium measurements of the motion of H and D atoms on a Pt(111) surface, enabling lower temperatures to be studied than were possible with QHAS[1]. Our data shows a broken Arrhenius dependence, indicating two transport regimes; high temperatures (>120 K) and low temperatures (<110K). Otherwise, the data shows good agreement with a single jump model.

Our results offer a comprehensive dataset that is a severe test of theory. We compare the experimental data to existing protonic band structure calculations[2]. For H, it is possible to relate the measured activation energies to transitions to specific excited states of H, suggesting the diffusion of H on Pt(111) proceeds by activated quantum tunnelling. For D, the correspondance is less clear. We see a large change in pre-exponential factors with temperature, but not isotope, which we relate to energy exchange between adatoms and the surface. We compare the apparent rates of hopping with the expected tunnelling and energy transfer rates, in order to identify the rate limiting proceses.

Recent work suggests that surface steps determine the macroscopic behaviour. However, our measurements are sensitive to the local, microscopic behaviour and give an alternative picture of the quantum motion[3].

[1] A. P. Graham, A. Menzel and J. P. Toennies, J. Chem. Phys. 111, 1676 (1999).

[2] S. C. Badescu, P. Salo, T. Ala-Nissila, S. C. Ying, K. Jacobi, Y. Wang, K Bedurftig and G.Ertl, Phys. Rev. Lett. 88, 136101 (2002).

[3] C. Z. Zheng, C. K. Yeung, M. M. T. Loy, and Xudong Xiao. Phys. Rev. Lett. 97, 166101 (2006).

Thin Film
Room: B4 - Session TF-WeA

ALD/CVD: Novel Applications, Mechanical Properties
Moderator: N.P. Guisinger, Argonne National Laboratory

2:00pm **TF-WeA1 ALD Applications to DNA Sequencing, Electrolytic Junctions and Nanofluidics**, ***S.M. Rossnagel***, *S.-W. Nam*, IBM T.J. Watson Research Center

One approach to sequencing DNA electrostatically pulls single-stranded DNA through a small, 2-3nm diameter aperture, also known as a nanopore. We have built and configured this electrolytic device with three 3 nm-scale electrodes and nanopores ranging from 15 to 1 nm with the goal of measuring the impedance of each nucleotide (C,G,A,T) as it passes through the nanopore. ALD films are critical to the fabrication at this dimension, and we have focused mostly on dielectric layers where conformality and pinhole-free deposition are critical. A related structure uses an ALD gate dielectric in a single electrode electrolytic device which functions as a pfet at sub 5nm range. (The source and drain are the upper and lower electrolte reservoirs). Electrical results show a modest gain (10x) in the range where debye shielding of the electrolyte is similar to the nanopore dimensions. This opens the ability to electrically switch conducting biological fluids at the nanoscale, and we have built devices to this end. The ALD-based approach can fabricate trench-based horizontal nanochannels down to 8nm diameter. These devices are fabricated using ALD of both metals and oxides in a keyhole structure based on trenches patterned by e-beam lithography.

2:20pm **TF-WeA2 Fabrication and Characterization of Point Contact Metal-Insulator-Metal Diodes for Potential Applications in Energy Harvesting**, ***P. Periasamy***, Colorado School of Mines, *A. Dameron, J. Bergeson, J. Berry, P. Parilla, D.S. Ginley,* National Renewable Energy Laboratory, *R. O'Hayre*, Colorado School of Mines

A **rectenna** is a device that can convert electromagnetic radiation such as **visible light to DC power** using a rectifier and an antenna component. Our focus in this paper is on fabrication and characterization of the rectifier component. **Metal-Insulator-Metal (MIM) diodes** are an excellent choice for the rectifier, since MIM diodes rectify via tunneling. Thus, a properly optimized MIM may be able to rectify signals in femto seconds (10^{-15} s), which enables rectification of visible light (400-790 THz). A **point contact MIM diode (PCD) configuration** is adopted in order to achieve the small diode capacitance necessary for high-frequency rectification. In the PCD, a planar metal/insulator bilayer “sandwich” is contacted by a second metal in the form of a sharp tip, resulting in a diode contact area as small as μm^2 – nm^2. For our initial studies we are using blunt wire tips, since our initial objectives are to optimize the planar metal/insulator layers. PCD devices with **different metal 1, insulator and metal 2 (wire tip) combinations were fabricated** and characterized for the desired I-V characteristics.

The PCD diodes were fabricated as follows. First, 100nm films of metal 1 candidates such as **Ni, Nb, Sm, Hf** were deposited by **DC sputtering**. The insulator layer (**NiO_X, NbO_X, SmO_X, HfO_X**) was grown by **anodization** of the metal films and by **atomic layer deposition**. Devices were characterized as a function of thickness of the insulator layer. In addition, dual insulators (MIIM) were grown and compared with single insulator (MIM) devices. TiO_2 and Al_2O_3 were used for the second insulator layer. The deposition parameters of the metal and the insulator films were optimized to obtain films that are pinhole free and have low surface roughness. The films were characterized using scanning electron microscopy, atomic force microscopy, x-ray reflectivity and x-ray photoelectron spectroscopy. Pt, Au and Ag wire tips were used for Metal 2. PCD IV characteristics were analyzed in terms of **non-linearity** (NL) $[(dI/dV)*(V/I)]$, **asymmetry** (AS), **responsivity** (RY) $[(d^2I/dV^2)*(dI/dV)]$ and **turn-on voltage** (TOV) [based on positive current]. From the matrix of different material combinations and the fabricated MIM devices, an attempt was made to identify critical parameters that influence the desired I-V curve characteristics.

The NL, RY and TOV values for the Nb-NbO_X (5.2 nm thick)-Pt system were 2.3, 3.8 A/W and 0.1 V respectively. But the AS value was not as good as found in Nb-NbO_X (22.81 nm thick)-Pt system. At the same time, however, the turn-on voltage was relatively higher (1.7 V) in the latter system. Such results would help us fabricate a diode suitable for solar energy harvesting.

2:40pm **TF-WeA3 Tungsten Oxide (WO_3) Thin Films for Application in Advanced Energy Systems**, ***S.K. Gullapalli***, *C.V. Ramana*, University of Texas at El Paso

Coal gasification plants are advanced energy production systems. Inherent processes in these plants produce a lot of hazardous gases, such as hydrogen sulfide (H_2S), which must be continuously and efficiently detected and removed before the syngas is used for power generation. The objective of the present work is to develop stable and reliable H_2S sensors based on nanostructured tungsten oxide (WO_3) thin films. The chemical sensing ability and high-temperature stability of WO_3 is the motivation for the work. WO_3 thin films have been fabricated by RF reactive magnetron-sputter deposition. A W-target has been employed for all the depositions and to investigate the effect of processing conditions on the growth and structure of resulting WO_3 films. The fabrication has been made under varying substrate temperatures (T_s), in the range 30(RT)-400 °C. The argon to oxygen flow ratio is kept constant at 1:6 for reactive deposition and oxide formation. Investigations made using x-ray diffraction (XRD) and scanning electron microscopy (SEM) indicate that the effect of T_s is significant on the microstructure of WO_3 films. XRD and SEM results indicate that the WO_3-films grown RT are amorphous, whereas films grown at higher temperatures are nanocrystalline. Thermally activated growth process of WO_3 films is evident in the data. The average grain size increases with increasing T_s. WO_3 films exhibit smooth morphology at lower temperatures (< 200 °C) while relatively rough at 400 °C. The optical measurements indicate that the films exhibit relatively high transmittance and the band gap is dependent on the grain-size. The analyses indicate that the nanocrystalline WO_3 films grown at 100-200 °C could be the potential candidates for H_2S sensor development for application in coal gasification systems.

3:00pm **TF-WeA4 Growth Kinetics in a Large-Bore Vertically-Aligned Carbon Nanotube Film CVD Process**, ***K. Bosnick***, *L. Dai*, National Research Council Canada

We installed and developed a large-bore CVD reactor for the growth of carbon nanotube materials on device substrates. The reactor was custom built by Tystar, Inc. and is capable of processing batches of up to fifty 150-mm wafers with industry-standard process controls. We synthesize vertically-aligned films of multi-walled carbon nanotubes by employing a Cr-Ni-Fe thin film catalyst stack pre-deposited on substrates. The kinetics of the growth process is studied by measuring the film thickness, the resistivity (indicative of the density), and the distribution of CNT diameters as a function of pre-growth catalyst treatment time, growth time, and growth temperature. It is found that pre-growth treatment times of about 200 min are needed before reaching steady-state catalyst conditions. Shorter pre-growth treatment times produce a more thick but less dense film. The CNT diameters are only weakly affected by the pre-growth treatment time (for at least greater than 30 min). A model is proposed to explain these results whereby the catalyst film quickly breaks up into catalyst particles but further treatment is needed to activate these particles. More activated particles leads to a more dense film but due to increased demand on feedstock also produces a less thick film. The kinetics of the film growth are studied as function of growth time and temperature under steady-state catalyst conditions.

4:00pm **TF-WeA7 Study of Silicon Strain in Shallow Trench Isolation**, ***M. Belyansky***, *N. Klymko, D. Chidambarrao, R. Conti, F. Liu*, IBM

Generation of strain in a silicon channel has been successfully used to increase performance of state of the art CMOS devices. The most studied methods are embedded silicon germanium, stress liners and stress memorization techniques. However, there have been relatively few studies of the effect of thin film dielectric materials in the Shallow Trench Isolation (STI) area on silicon strain.

Raman spectroscopy has been used as a primary tool to measure silicon strain on a variety of STI structures. Different STI dielectric gap fill materials have been evaluated including high density plasma CVD, sub-atmospheric CVD and spin-on glass based oxide thin films. It has been shown that both intrinsic stress of thin film dielectric material and STI structure type affect strain in silicon. Ways of introducing new dielectric gap fill materials and generating high stress in STI are discussed including the effect of the STI CVD liner material on Si strain.

Advantages and limitations of Raman based strain metrology in the semiconductor industry are delineated. Raman spectroscopy showed much better sensitivity to Si strain compared to TEM based strain measurement techniques.

The findings have been confirmed electrically on CMOS devices with tensile and compressive strain in STI region. Substantial improvement in pFET transistor performance has been demonstrated for devices with tensile dielectric in STI.

4:20pm **TF-WeA8 Critical Compressive Stress for Cracking of Al_2O_3 ALD Films**, ***S.H. Jen***, *J.A. Bertrand, S.M. George*, University of Colorado

Flexible displays require various thin films that must withstand stress without cracking. Very little is known about the critical stress for cracking for ALD films for either tensile or compressive stress. The critical stress for cracking is particularly important for the design of gas diffusion barrier films on polymer substrates. Flexible organic light emitting diodes (OLEDs) require barriers with extremely low water vapor transmission rates of < 1 x 10-6 g/m2/day. Film cracking will severely impair the gas diffusion barrier.

Compressive stress can be applied by depositing films at elevated temperature on a high thermal expansion substrate and then letting the sample cool to room temperature. The critical compressive stress for cracking of Al2O3 ALD films was determined using Teflon FEP which is a polymer with a high thermal expansion coefficient. Different compressive stresses were defined using different deposition temperatures. Crack densities were visualized using scanning electron microscopy (SEM) images. The critical stress for cracking was determined for various Al2O3 ALD film thicknesses.

Al2O3 ALD film thicknesses were examined from 19-48 nm. The SEM images showed that the films buckled and then cracked with increasing compressive stress. The critical stress for cracking was constant at ~2 GPa for the thicker films with thicknesses >30 nm. The critical stress for cracking increased dramatically to >4 GPa for film thicknesses < 20 nm. These results indicate that thinner Al2O3 ALD films are more flexible and able to withstand higher compressive stresses without cracking. Enhanced multilayer gas diffusion barriers should employ thin Al2O3 ALD layers for optimum flexibility.

4:40pm **TF-WeA9 Elaboration of Dichroic Filters on Shape Memory Substrate**, ***O. Carton***, *M. Lejeune, A. Zeinert,* Laboratoire de Physique de la Matière Condensée, France, *S. Zaidi, F. Lamarque*, Laboratoire Roberval, France

The aim of this work is the elaboration of thin films for optical filtering under mechanical constrains. Our dichroic filters (transmission of one wavelength and reflection of another one) had to be deposited on shape memory substrates, with respect to several conditions:

- low thickness of the filter in order to minimize the weight supported by the substrate
- low internal stress in the structure to limit the mechanical action of the filter on the substrate
- high elasticity in order to preserve a good adhesion when the substrate is strongly deformed
- low light absorption in order to transmit the maximum of energy

The realised structures were made up of the stack of two couples of materials: amorphous hydrogenated silicon (a-Si:H) / silicon dioxide (SiO_2), and a-Si:H / amorphous polyacid methacrylic (a-pAM), using the Bragg reflector structure with seven layers only. These materials have been elaborated using two plasma techniques: a-Si:H and SiO_2 were deposited by magnetron sputtering and the polymeric layers were deposited by inductive plasma enhanced chemical vapor deposition (PECVD). A brief study of the optical properties as a function of the deposition parameters has been performed for each material, and the chemical structure of the polymer was investigated with FTIR as a function of the RF power forwarded to the plasma. The internal stress of the optical filters has been calculated using the Stoney formula, and structures made up with polymeric layers have shown better mechanical properties than structures with silicon dioxide, with a lower value of residual stress. The elasticity of the realized optical filters has been tested on plastic substrate with a repeatedly deformation applied to the structure, and a good stability has been observed with no significant change in the optical filtering properties before and after the deformations.

The aimed application of these filters is to achieve a chromatic wireless control of shape memory alloy (SMA) micro-actuators. The actuation is performed by the use of two laser sources in order to heat and distort pieces of SMA (Nitinol). This chromatic response was first realised with optical filters on glass substrate, the Nitinol pieces were placed under this glass substrate and the selective response for the different laser wavelengths was observed. Then the optical filters were directly deposited on Nitinol sheet and the selective response was also visualized.

5:00pm **TF-WeA10 Single-Stage Deposition of Organic/Inorganic Multilayer by Plasma Enhanced and Initiated Chemical Vapor Deposition**, ***A.M. Coclite***, University of Bari, Italy, *G. Ozaydin-Ince,* Massachusetts Institute of Technology, *F. Palumbo, R. d'Agostino,* University of Bari, Italy, *K. Gleason*, Massachusetts Institute of Technology

Deposition techniques of multiple dense, inorganic layers alternated with soft, organic ones are widely investigated for several technological applications. Generally, a combination of two different deposition techniques is employed for deposition of organic/inorganic multilayered coatings. The possibility of a single-chamber vacuum-deposited system may greatly simplify the production and allows the quicker and cheaper roll-to-roll deposition. Here we propose a new technique for multilayer deposition, consisting of coupling initiated and plasma enhanced CVD, maintaining the same organosilicon precursor and the same reactor configuration.

Multilayer coatings comprised of alternating inorganic (silica-like) and organic (organosilicon polymer) layers were deposited using hexavinyldisiloxane (HVDSO) as precursor. The organosilicon polymers were deposited by initiated CVD (iCVD) at filament temperature of 280°C. The silica-like layers were obtained by Plasma Enhanced CVD (PECVD) applying RF power to the same filament used in the iCVD process. The multilayers were obtained through layer by layer deposition, switching from one technique to the other without venting the system.

Chemical and morphological characterization of the organic single layer showed that the iCVD of poly-HVDSO resulted in a very crosslinked film with high deposition rate, high Carbon content (79 % from XPS analysis) and very low roughness (0.7 nm). PECVD of the same monomer, when highly diluted in Oxygen, gave inorganic coating with a low content of OH terminal groups and high deposition rate. X-ray photoelectron spectroscopy (XPS) depth profile, ellipsometric characterization and Secondary electron microscopical imaging of multilayer coatings clearly showed that the various layers do not mix or interdiffuse, but maintain the same chemical composition and refractive indices as in single layers deposition. When the inorganic layer was deposited over the organic layer a graded interphase (around 40 nm thick) was detected, due to plasma ion bombardment of the underlayer.

The advantage of coupling iCVD and PECVD consists in the possibility of having dense inorganic coatings alternated with organic interlayers characterized by high crosslinking and high C content. Moreover the high smoothness of the iCVD layer is important to reduce the roughness of the under-layers in order to limit the formation of defects in the successive inorganic up-layer. Hence, all this properties make this kind of multilayer coatings promising as ultrahigh barriers (UHB) against the transmission of water vapor and oxygen through polymer substrates.

5:20pm **TF-WeA11 The Role of Ammonia as an Inhibitor Species in Low Temperature CVD to Reduce Film Growth Rate and Enhance Conformal Coverage**, ***S. Babar***, *P. Zhang, W. Wang, N. Kumar, J.R. Abelson*, University of Illinois, Urbana-Champaign

Our group recently demonstrated the phenomenon of growth inhibition in low temperature chemical vapor deposition of TiB_2: a neutral molecule is added to the flow of precursor in order to reduce the growth rate and enhance the degree of conformal coverage; the atoms contained in the inhibitor are not incorporated into the film [JACS **130**, 52 (2008)]. Here, we demonstrate the inhibition behavior of ammonia on HfB_2 growth using $Hf(BH_4)_4$. The growth rate and surface roughness are measured in-situ by spectroscopic ellipsometry. At substrate temperatures below 350°C, ammonia reduces the growth rate of HfB_2, down to zero at an ammonia pressure of ~ 1 mTorr. Upon cessation of the ammonia injection, growth resumes after 1-2 minutes. When ammonia is delivered as short pulses, the surface roughness appears to increase, then declines again after the ammonia is pumped out. We explore the origins of this phenomenon, which may involve the formation of a dielectric surface layer or re-nucleation of HfB_2 growth. We explain the role of ammonia using a site-blocking model in which ammonia adsorbs reversibly on the surface sites and reduces the rate of precursor adsorption. This simple rate model fits the data well. We show that growth inhibition by ammonia can be used to greatly enhance the degree of conformal coverage in a deep trench.

5:40pm **TF-WeA12 Nanoscale Engineering of Ceramic Supports for High Permeance Ultrafiltration Membranes**, ***R. Nahm***, *P.C. Rowlette, C.A. Wolden*, Colorado School of Mines

Anodized aluminum oxide (AAO) membranes are commercially available supports that offer a high pore density and a narrow pore size distribution. In this talk, we describe the use of pulsed plasma-enhanced chemical vapor deposition (PECVD) to modify AAO supports for arbitrarily designed molecular weight size cutoffs. Pulsed PECVD is a self-limiting deposition technique that provides digital control over the amount of deposited material (i.e. 1 Å/pulse). Specifically, we use pulsed PECVD to deposit SiO2 at room temperature to affect arbitrary pore size control. For this work, pulsed PECVD is operated in a nonconformal mode, meaning that only the very pore opening is modified with no deposition occurring throughout the majority of the structure. Modified membranes are characterized by atomic force and electron microscopies. An advantage of this approach is that the modifications can be done very quickly. In addition, we demonstrate that the nominal pore size may be significantly reduced without any impact on the permeance. Moreover, these membranes provide a well-defined geometry that provides a unique experimental platform for studying hindered transport and nanofluidics. The modified membranes are characterized by gas permeance, water permeance, and measurements of solute rejection. SiO2 is the material of choice since it may be readily modified through addition of self-assembled monolayers to control the hydrophilicity of the surface and enhance biocompatibility. We will present preliminary work in this regard as well.

Tribology Focus Topic
Room: C4 - Session TR+SE-WeA

Advances in Surface Engineering for Friction and Wear Control

Moderator: S.S. Perry, University of Florida

2:00pm **TR+SE-WeA1 The Deposition of Highly Adherent Fullerene-Like CN$_X$ Coatings on Steel Substrates of Complex Geometry**, ***E. Broitman***, Linköping University, Sweden & Carnegie Mellon University, *S. Schmidt, G. Greczynski,* Linköping University, Sweden, *Zs. Czigany,* Research Institute for Technical Physics and Materials Science, Hungary, *C. Schiffers,* CemeCon AG, Germany, *L. Hultman*, Linköping University, Sweden

Due to their superior wear resistance, high hardness, and low friction coefficient, carbon nitride (CN$_x$) coatings have been proposed as a candidate to replace diamond-like carbon (DLC) coatings. In this study we present the structural, morphological, and adhesive properties of fullerene-like (FL) and amorphous carbon nitride (CN$_x$) coatings synthesized by HIPIMS in an industrial CC-800/9 CemeCon equipment. The coatings were grown on steel substrates of complex geometry (including those with small diameter cavities and holes, and shapes such as bolts, nuts, and screws) to thickness of 2-3 µm. A novel HIPIMS pretreatment with two HIPIMS power supplies was used to increase the adhesion of the coatings: one power supply to establish the discharge and one to produce a pulsed substrate bias. The environment of the created Cr plasma sputter-cleans the surface and forms a Cr-containing gradual interface into the substrate. Subsequently, carbon nitride coatings were prepared by HIPIMS from a high purity graphite target in a N$_2$/Ar discharge at 3 mTorr with the N$_2$ fraction varied from 0 to 1, and the substrate temperature varied from ambient to 300 °C. X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), scanning transmission microscopy (STEM), and high resolution transmission electron microscopy (HRTEM) have been used to study the coating and the steel/Cr/CN$_x$ interfaces. Identification of coating adhesion failures was done by the Daimler-Benz Rockwell-C adhesion test.

2:20pm **TR+SE-WeA2 Tribological and Mechanical Properties of Nanostructured Hydrogenated Amorphous Carbon and TiB2 Films**, ***B. Zhao***, *Y.W. Chung*, Northwestern University

Hydrogenated amorphous carbon films (CHx) are known to attain ultra-low friction performance only in dry environments. Our work demonstrated that sulfur doping of hydrogenated carbon films (CHx+S) 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 nanostructured films of CHx (or CHx+S) 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 as well as tribological and mechanical properties. Nanolayered films with a majority titanium diboride composition showed hardness improvement around rule-of-mixtures values with favorable low friction performance in humid air.

2:40pm **TR+SE-WeA3 Tribological Characteristics of a Tungsten Tip/ Au-Ni Alloy Interface, Studied by Means of Combined STM-QCM**, ***L. Pan***, *J. Krim*, North Carolina State University

A two-phase Au-Ni (20 at.% Ni) alloy has recently been suggested as a potential contact material for RF switch microelectromechanical systems (MEMS) switches. Tribological properties impact switch closure behaviour and heating at the interface impacts both the electrical and mechanical properties of the switch. We have thus performed a QCM STM study of heating and wear at the interface between a tungsten tip and a range of gold nickel alloys with varying compositional percentages.The comparison of nano heating generated via friction and surface response to the tip crash would be shown here.

3:00pm **TR+SE-WeA4 Quantitative Measurements of Adhesion Forces in Polycrystalline Silicon Surfaces via a Doubly Clamped Beam Test Structure**, ***I. Laboriante***, *B. Bush, G. Li, C. Carraro, R. Maboudian*, University of California - Berkeley

Current state of knowledge indicates that the prevalence of static adhesion in microstructures remains one of the major hurdles preventing a larger number of MEMS-based products from entering the mainstream, and quantitative understanding of this phenomenon is currently lacking. This is due to the fact that contact mechanics at the micro-/nanoscale are a complicated multiscale problem, in particular when one is dealing with rough and rigid impacting surfaces. The results of investigations aimed at elucidating the adhesion force between co-planar, impacting polycrystalline silicon surfaces will be presented using a microfabricated doubly clamped cantilever beam test structure. The effect of apparent area of contact will be examined via microfabricated dimples of varying size. Determination of adhesion forces through systematic optical interferometric measurements will be presented. The data reveal a weak dependence of adhesion on the apparent contact area, instead of scaling with the contact area. Possible mechanisms leading to this behavior will be discussed.

4:00pm **TR+SE-WeA7 Nanoscale Control and Understanding of Friction at High-Speeds for Future Disk Drive Head-Disk Interfaces**, ***C.M. Mate***, Hitachi San Jose Research Center **INVITED**

Tremendous progress has been made over the past several decades towards understanding the nanoscale origins of tribological phenomena [1], leading to numerous breakthroughs in friction and wear control. The impact of these breakthroughs has been particularly striking in the disk drive industry, where improved tribological engineering of the head-disk interface has led to the magnetic spacing being reduced from ~100 nm in 1995 to ~10 nm in 2009, enabling a 10^3 increase in storage areal density. In today's drives, recording head sliders fly reliably at incredibly small clearances (~2 nm during read-write operations) for many years at speeds > 10 m/s. As the industry moves to even smaller spacings, however, head-disk contact will become more frequent and improved surface engineering to control friction and wear will become more paramount.

In this talk, I will first review the key surface engineering features (slider air bearing surface, disk topography, overcoat, lubricant, etc.) that enable today's disk drive sliders to fly at nanometer clearances over disk surfaces. I will then describe work going on in our laboratory both to determine the nanoscale origins of friction and to use this understanding to develop future head-disk interfaces that are expected to run in continuous contact.

To determine the nanoscale origins of friction at high-speed sliding contacts (> 1 m/s), we have developed a *high shear rate apparatus* using technology from the disk drive industry [2]. With this new instrument, friction, adhesion, and wear can be studied at high sliding speeds (1 to 100 m/s) for nanometer thick lubricant films sandwiched between atomically smooth surfaces. Recently, this instrument has been modified to incorporate optical microscopy for in-situ visualization when a slider runs in contact with a transparent rotating disk. This technique has been particularly useful for studying the formation of nanoscale, non-equilibrium menisci at high speed contacts.

[1] C.M. Mate, Tribology on the Small Scale: A Bottom up Approach to Friction, Lubrication, and Wear, Oxford University Press, Oxford, 2008.

[2] C. M. Mate, R.N. Payne, Q. Dai, K. Ono, *Phys. Rev. Lett.* 97 (2006) 216104.

4:40pm **TR+SE-WeA9 The Effects of Humidity on the Tribological Properties of Nanocrystalline Diamond**, ***N. Theodore***, *K.J. Wahl*, Naval Research Laboratory

The tribological response of nanocrystalline diamond (NCD) coatings to variations in moisture content of the environment was examined under reciprocating sliding conditions. Surface roughness, structure, composition, and carbon chemistry were determined by atomic force microscopy (AFM), X-ray diffraction (XRD), and Raman spectroscopy. All coatings were nanocrystalline with crystallite sizes ranging from to 4 to 60 nm as measured by XRD. Visible wavelength Raman spectroscopy of the NCD coatings revealed various carbon chemistries. The NCD coatings could be classified in three subsets by Raman microscopy: (1) coatings exhibiting a single strong peak at 1332 cm^{-1} typical of crystalline diamond bonding; (2) coatings possessing broad peaks at 1340 cm^{-1} and 1550 cm^{-1} characteristic of the *D* and *G* peaks in sp^2 hybridized carbon along with the diamond 1332 cm^{-1} peak; and (3) coatings displaying additional peaks at 1135 cm^{-1} and 1470 cm^{-1}, commonly attributed to trans-polyacetylene bonding, along with the three previously described peaks. Reciprocating sliding tests using sapphire counterfaces in controlled humid environments resulted in low friction values for all coatings, between 0.02 and 0.09. Decreasing the humidity caused an increase in the number of cycles to run-in to low friction. These observed differences in run-in and counterface wear as a function of environment will be presented and related to NCD coating composition and microstructure.

5:00pm **TR+SE-WeA10 Crystallography-Dependent Self-Lubrication on Nickel Surfaces During Wear***, **C.C. Battaile**, S.V. Prasad, J.R. Michael, P.G. Kotula*, Sandia National Laboratories

Wear experiments on Ni surfaces show that stable, nanocrystalline tribofilms can form under appropriate tribological conditions, even on single crystals. The presence of these nanocrystalline layers is qualitatively dependent on the crystallography of the surface and wear orientations, and are responsible for a marked reduction in friction on bare contact, suggesting numerous surface engineering possibilities. For example, when a 1 N normal load and 3.75 mm/s tangential speed are applied to a 1/8" diameter Si3N4 ball in contact with electropolished single-crystal Ni in a dry nitrogen environment, the measured friction coefficient is usually in the range 0.6 to 0.8. However, when the Ni surface is of the {110} type and the sliding direction is <211>, the friction coefficient abruptly drops to 0.3 after about 500 cycles, where it remains indefinitely. Modeling of this phenomenon, based on crystal plasticity, microstructure formation, and grain boundary sliding, suggests that the self-lubrication is due to the capacity of ultra-fine-grained microstructures to support grain rotation. Wear experiments on bulk nanocrystalline Ni deposits support this hypothesis by demonstrating low friction coefficients (around 0.3) and virtually no wear-in under low loads and sliding speeds, and higher friction (around 0.6) under high loads and speeds. We will provide an overview of the experiments and modeling of nanocrystalline film formation on single-crystal Ni, detail the results from friction experiments on bulk nanocrystalline Ni, and discuss model validation of the phenomenon's strain rate sensitivity.

5:20pm **TR+SE-WeA11 NEXAFS Characterization of Vapor Deposited Monolayer and Submonolayer Films on Si and Al_2O_3 for MEMS Friction Control***, **C. Jaye**, D.A. Fischer,* National Institute of Standards and Technology*, B.M. DeKoven,* Surface and Interface Consulting*, J.D. Chinn*, Integrated Surface Technologies

Most microelectromechanical systems (MEMS) are fabricated using semiconductor and ceramic materials such as Si, and SiO2, and Al2O3 which are hard, brittle materials and are not commonly used for mechanical devices. MEMS components are very small and lack power or much inertia when in motion, so they are highly susceptible to the influence of adhesive and surface forces. MEMS lubrication schemes involving vapor phase lubrication have been proposed as a means of continuously replenishing lubricant films on MEMS surfaces.

We present synchrotron based near edge x-ray absorption fine structure (NEXAFS) spectroscopy results of vapor deposited monolayers and submonolayers on SiO2 and Al2O3 substrates under different process conditions. NEXAFS is a powerful non-destructive method in which soft x-rays are absorbed followed by the excitation (transition) of electrons from a core K- or L-level to partially filled into empty low-lying antibonding molecular states. Bond orientation information is deduced from the changes in the intensity of the resonances upon rotating the substrate normal in the plane of incidence of the polarized synchrotron beam.

Carbon K-shell NEXAFS performed at different incidence angles revealed that the vapor deposited fluorodecyltrichlorosilane (FDTS) molecules on silicon and alumina substrates produced self-assembled monolayered films that have high surface coverage and can be highly oriented. Using the NEXAFS technique, dichroic ratios (based on the **σ*C-F** resonance) of the order of 0.5 have been obtained, thus revealing that these FDTS films have a high degree of molecular orientation. Orientation and coverage comparisons for water wiped and isopropylalcohol wiped FDTS as well as directly vapor deposited FDTS will be presented. The implications for the design of surfaces and interfaces for stiction control in MEMS devices will also be discussed.

Vacuum Technology
Room: J1 - Session VT-WeA

Modeling and Accelerators
Moderator: M. Stutzman, Jefferson Lab

2:00pm **VT-WeA1 Slit Flow Simulation using Non-Linear BGK and ES-Models***, **I.A. Graur**, A. Polikarpov*, Provence University, France

The flow through a two-dimensional slit is simulated using non-linear model kinetic equations (BGK, ES-model) in the large Knudsen number range. The discrete velocity method is implemented to determine the flow parameters. Several different (finite and infinite) tank pressure ratios are considered and are compared with the results of DSMC simulations and some experimental data.

2:20pm **VT-WeA2 Background Reduction Strategies for Angular Profile Measurements of Gas Injected in Ultra-High Vacuum***, **L.J. Isnard**, R.M. Arès*, Université de Sherbrooke, Canada

Ultra-high vacuum (UHV) based deposition techniques, such as molecular beam epitaxy (MBE) and chemical beam epitaxy (CBE), have stringent requirements on layer thickness and composition uniformity. Concurrently, the source use efficiency is usually very low and needs to be improved while maintaining the same level of uniformity. There is therefore a need for a precise and reliable simulation platform to predict the angular distribution of gas molecules injected in vacuum through a nozzle of a given geometry. Several calculation techniques have already been proposed for MBE [1-6] and CBE [7].

However, the validity of such models needs to be established through a systematic experimental study that clearly isolates the contributions of each parameter. For this purpose, a test platform dedicated to the measurement of molecular beam angular profiles produced by a nozzle in UHV was designed and built. Its main features are discussed, especially regarding its ability to produce precise and reproducible data. For profiles being measured far away from the injector, the unwanted contribution from the molecules that reach the sensor after being scattered by the chamber walls (i.e. background level) is fairly large. In order to reduce it, several design strategies are considered and evaluated on the basis of the theory of rarefied gas dynamics. In particular, an innovative approach based on an angular selection tube is presented with a quantitative evaluation of its effect on the signal to background ratio. Finally a rule of thumb is proposed for the choice of the tube's dimensions allowing a maximum background reduction while keeping the impact on the signal as small as possible.

[1] J. A. Curless, J. Vac. Sci. Technol. B 3, 531 (1985).

[2] Z. R. Wasilewski, G. C. Aers, A. J. SpringThorpe, and C. J. Miner, J. Vac. Sci. Technol. B 9, 120 (1991).

[3] K. T. Shiralagi, A. M. Kriman, and G. N. Maracas, J. Vac. Sci. Technol. A 9, 65 (1991).

[4] Yu. N. Grigor'ev, M. Sh. Shavalev, and V. P. Shapeev, Tech. Phys. 39, 759 (1994).

[5] E. V. Ozolova, I. V. Igrat'ev, and A. P. Abramov, Tech. Phys. 39, 957 (1994).

[6] S. Kincal and O. D. Crisalle, Proc. Am. Control. Conf. 6, 4001 (2000).

[7] L. Isnard and R. Arès, J. Crystal Growth 311, 1640 (2009).

2:40pm **VT-WeA3 Investigation of Vacuum Flows in Fusion Reactors***, **S. Varoutis**, V. Hauer, C. Day*, Forschungszentrum Karlsruhe (FZK), Germany

Vacuum flows are strongly connected to several subsidiary systems of fusion reactors. In particular, there are high vacuum pumping systems for evacuation and maintenance of the needed low pressure levels in the torus, in the cryostat and in the neutral beam injectors. Each vacuum system consists of networks of various channels with different lengths and cross sections. The flow in such channels varies from the free molecular regime up to the hydrodynamic limit. In the present work, an experimental setup for measuring the mass flow rate of gases is proposed. Its principle is based on the predefined conductance through the duct and the measurement of the corresponding pressure difference. Experimental data for channels with various lengths and cross sections are presented and compared with corresponding numerical results based on the linearized kinetic BGK equation and the direct simulation Monte Carlo method (DSMC). It is noted that in all cases a very good agreement between experimental and numerical approaches, is observed.

3:00pm **VT-WeA4 Accurate Measurements of Low Permeation Flows of Hydrogen**, ***V. Nemanic***, *B. Zajec, M. Zumer*, Jozef Stefan Institute, Slovenia

Permeation of hydrogen isotopes from the upstream pressure through a membrane into high vacuum at elevated temperatures is a challenging task for vacuum technology when very low flows must be determined. The detection limit and accuracy of results depend on several experimental details. Geometrical and mechanical constraints set an engineering issue since the ultimate tightness of seals at high temperature must be preserved. On the other hand, measurements of the steady permeation flux and its transients require high sensitivity and stability of the gauges. It is also essential that the background represents only a fraction of the signal. We present recent improvements applied on a permeation cell design that results in efficient background suppression. When implemented in an all-metal UHV system, low permeation fluxes down to 10^{-11} mbar L/(cm^2 s) could be measured. We also present an innovative technique to perform measurements at a low upstream pressure capable of detecting changes corresponding to a permeation flux as low as 10^{-14} mbar L/(cm^2 s). The interpretation of data is presented by the surface rate constants rather than by diffusivity and solubility since the permeation regime at low pressures is known to be limited by surface reactions. Better experimental capability is needed today in the hydrogen storage technology and also in the field of nuclear fusion reactors to study the efficiency of permeation barriers and to predict tritium retention in the walls.

4:00pm **VT-WeA7 Vacuum R&D at Cornell Towards to Cornell Electron Storage Ring Test Accelerator for ILC Damping Ring and the ERL-based Light Sources**, ***Y. Li***, Cornell University **INVITED**

Many research and development efforts in the vacuum technology front in supporting two major research programs at the Cornell Laboratory for Accelerator Based-Sciences and Education (CLASSE). Over the past 3 years, a prototype DC photo-cathode injector was designed and constructed at CLASSE, as a key initial step towards to the Energy Recover Linac (ERL) based light sources at Cornell. The prototype injector includes a DC photo-cathode electron gun, a 10-cell superconducting radio-frequency cavity cryo-module, electron beam transporting beamlines equipped with a suit of beam instrumentation and electron beam dumps. Among various challenges, achieve and maintain extreme high vacuum in the DC photo-cathode electron gun is essential to the success of the prototype injector project. In the past year, we have also successfully re-configured the Cornell Electron Storage Ring (CESR) vacuum system to convert it into a test accelerator (thus CesrTA), as a part of the Globe Design Efforts (GDE) of the International Liner Collider Damping Ring. One of the goals is to understand electron cloud growth in vacuum chambers with many in-vacuum instruments of unique low-profile design, and to explore various eletron cloud suppression methods, including coatings of interior surfaces of vacuum beampipes. In this talk, highlights of the vacuum R&D efforts related to the two research programs are discussed.

4:40pm **VT-WeA9 Amorphous Carbon Films for the Eradication of Electron Cloud Effects in Modern Particle Accelerators**, ***P. Chiggiato***, CERN, Switzerland

High-intensity and high-energy positively charged beams could engender high density electron clouds in vacuum chambers. As a result, several detrimental effects could arise, such as beam instability, pressure increase and, at cryogenic temperatures, excessive thermal load. Among the crucial factors, the secondary electron yield (SEY) of the beam pipe material plays an important role: only when it is higher than a well defined threshold, the electron cloud build-up is possible. As an example, a value of 1.3 has been calculated for the Large Hadron Collider (LHC) nominal beam. Coating the whole vacuum chamber with a low SEY material is an attractive solution to this accelerator performance limitation.

Low maximum SEY have been reported for Ti-Zr-V non-evaporable getter films following in-situ heating. However, heating is not always possible. To cope with this constraint, sputtered amorphous carbon thin films have been studied for the unbakeable vacuum system of the Super Proton Synchroton (SPS), namely the largest LHC injector. After exposure to air for a few hours, the produced coatings show maximum SEY of about 1. In general, the yield increases for a longer exposure to air, but it can be kept lower than the threshold providing the coating parameters are suitably selected. UHV compatibility has been also studied and the relationship between outgassing rate and coating parameters has been highlighted.

The encouraging results obtained for small samples and a few vacuum chambers installed in the SPS vacuum system have triggered a programme possibly leading to the implementation of a-C films in the whole SPS (about 7 Km which amount to roughly 600 vacuum chambers); such a large scale application will be presented and the production strategy depicted.

5:00pm **VT-WeA10 Update on Pressure Simulation of Vacuum System at NSLS-II Storage Ring**, ***M.J. Ferreira***, *H.C. Hseuh, J.-P. Hu*, Brookhaven National Laboratory

National Synchrotron Light Source II (NSLS-II) will be a 3-GeV, 792-meter circumference, 3rd generation synchrotron radiation facility, with ultra low emittance electron beams and extremely high brightness X-ray beams. The storage ring vacuum system has a simulated average operating pressure of less than 1x10-9 mbar. A summary of the updated vacuum system design will be presented, based on outcome from pressure simulation using window-version Monte-Carlo based MOLFLOW+ code. The versatile PC-compatible code provides increasing details in pressure distribution of residual gases in the vacuum system, particularly for those active species scattering at innards of high-power and small-gap insertion devices. Since low emittance for electron beam is expected to achieve when proposed damping wigglers are installed at storage ring, a fine segmentation of code input at such critical sections will be processed to evaluate details from calculated pressure profile.

*Work performed under auspices of the United States Department of Energy, under contract DE-AC02-98CH10886

5:20pm **VT-WeA11 Fabrication of NSLS-II Storage Ring Vacuum Chambers**, ***H.C. Hseuh***, *L. Doom, M.J. Ferreira, C. Longo, P. Settepani, K. Wilson*, Brookhaven National Laboratory

National Synchrotron Light Source II (NSLS-II), being constructed at Brookhaven, is a 3-GeV, 500 mA, 3rd generation synchrotron radiation facility with ultra low emittance electron beams. The storage ring vacuum system has a circumference of 792 m and consists of over 250 vacuum chambers ranging from 1 m to 6 m in length, and an average operating pressure of less than $1\text{x}10^{-9}$ mbar to minimize beam-residual gas interactions. Most vacuum chambers are made of aluminum and stainless steel, with different cross sections either fitted into the bending magnets or surrounded by multipole magnets. The layout of the storage ring vacuum systems will be presented. The detailed design of the vacuum chambers, the pumps and the photon absorbers will be described. The aluminum chambers are extruded, curved with 25 m radii in the case of the bending chambers, precision machined and welded to bi-metal Conflat flanges using robotic welding machines. The fabrication and evaluation of these aluminum chambers will be presented.

*Work performed under auspices of the United States Department of Energy, under contract DE-AC02-98CH10886

5:40pm **VT-WeA12 The Vacuum System of the 3 GeV Taiwan Photon Source**, ***J.R. Chen***, NSRRC and NTHU, Taiwan, *G.Y. Hsiung, C.C. Chang, C.L. Chen, C.K. Chan, H.P. Hsueh, C.M. Cheng, C.Y. Yang*, National Synchrotron Radiation Research Center, Taiwan

A design and prototype of the vacuum system of a low-emittance 3 GeV synchrotron light source, the Taiwan Photon Source (TPS, with a circumference of 518.4m), is described. The TPS vacuum system has low-outgas aluminum beam ducts, low impedance structure, oil-less pumping system and oil-less fabrication process. Little dust, a stable mechanical structure and high reliability components are also equipped in the vacuum system. A 14 m long prototype of the TPS vacuum system was fabricated. Two 4 m long bending-magnet chambers were made by the CNC machining process, lubricated with ethyl alcohol to protect the aluminum surface from oil contamination. Ozonated water cleaning process was applied to reduce the photo-desorption rate from the chamber surface. The design considerations, the critical factors in fabrication and the test results of the vacuum system prototype are presented.

Applied Surface Science
Room: C2 - Session AS1-ThM

Advances in Surface Analysis
Moderator: J.A.N.T. Soares, University of Illinois, Urbana-Champaign

8:00am **AS1-ThM1 XPS – A Problem with Charge Referencing Non-Conductive Samples and Native Oxides***, **V. Crist***, XPS International LLC

Binding energies (BE) from non-conductive samples and native oxides are commonly charge referenced to the C 1s BE of the hydrocarbon peak of adventitious carbon that appears on the surface of all materials exposed to air. Various studies of the usefulness of this method have been carried out (r.f. P. Swift, **J. Surf. Interfac. Analysis**, p.47, 1982) and none have revealed any significant problem with this everyday practice.

In this talk, C 1s, O 1s and metal spectra and BEs from native and pure binary metal oxides (e.g. MgO or Y_2O_3), and a series of residual gas capture studies, will show that there is indeed an obvious and significant problem when this practice is applied to binary metals oxides known to have highly polarized bonds or states (i.e. Al, Cd, Ga, Hf, Mg, Sc and Y). The hydrocarbon C 1s BEs for these native metal oxides routinely appear above 286.0 eV, which is significantly greater than the 284.6-284.8 eV that is commonly used. Another set of native metal oxides (i.e. Ag, Be, Co, Ge, Pb, Si, Zn and Zr) have C 1s BEs: 285.5 eV < C 1s < 286.0 eV.

This higher than expected BE problem is sometimes found for carbon captured by freshly cleaned pure metals exposed (>10 hr) to residual UHV gases and the surface contaminants that adhere to nearby, unclean regions of the sample. The cause of these high BEs might be related to strong surface dipole moments (image potentials) that protrude outward from the highly polarized metal-oxide bonds or states of the metal oxide layer that lie just under the adventitious carbon over-layer. Strong surface dipole moments are predicted (by A. Zangwill, *Physics at Surfaces*, Cambridge Press, 1988) to extend several tens to hundreds of angstroms above the surface of metal oxides into the carbon over-layer and the vacuum, whereas dipoles from pure clean metals are predicted to extend only a few angstroms above the surface.

To demonstrate this problem, spectra from grounded native oxides are compared to native oxides that were floated and irradiated with a flood gun set to OFF, 2 eV and 15 eV (using Mono-XPS). An overlay of five Al 2p spectra (from a 1978 synchrotron study) shows the progressive growth of Al_2O_3 where the Al 2p BE for Al_2O_3 = 75.7 eV, **not** 74.3 eV as determined by averaging 42 BEs from pure Al_2O_3 BE values that are stored in the on-line NIST XPS database of BEs (SRD20). The mean NIST value is ~1.4 eV lower than the 75.7 eV found for native Al_2O_3 on kitchen foil that gives a 286.3 eV C 1s BE, and also the 75.5 eV found in the 1978 synchrotron study. The experimentally measured 286.3 eV value is 1.5 eV larger than the 284.8 eV value recommended by the NIST database, handbooks and instrument makers.

8:20am **AS1-ThM2 A New Web-Based System for Identifying Molecules and Molecular Structure using G-SIMS and SMILES***, **I.S. Gilmore***, *M.A. Phillips, F.M. Green, T.S. Salter, M.P. Seah*, National Physical Laboratory, UK

G-SIMS[1] is a powerful method for the identification of organics and complex molecules at surfaces. For complex molecules, evaluating the molecular structure can be key to correct identification. We have shown[2,3] that the molecular structure may be reassembled from fragment ions by studying the evolution of G-SIMS intensities as the surface plasma, with effective temperature T_p, is varied, known as G-SIMS-FPM. Recently, we have developed a novel approach[4], based on SMILES[5] (Simplified Molecular Input Line Entry Specification), to assist the reassembly process in an automated way through evaluation of the fragmentation pathways for given molecular structures. A computer program takes a parent structure and goes through every possible fragmentation to provide a tree structure of fragmentation products and simulated fragmentation pathways. For any fragment it is then possible to identify the molecular structure, its mass and a pathway to the parent. We find that there is a good correlation with peak evolution in G-SIMS-FPM data and simulated pathways for two amino acids and a simple peptide. This significantly enhances the application of G-SIMS-FPM to unknown materials. Once fragmentation pathways have been calculated for a molecule they are added to a library.

We have now developed an informatics database system with a web-based front-end that allows analysts to generate fragmentation pathways for any molecule in SMILES format. For new molecules, the pathways are added to the library. Analysts may then explore the fragment pathways for comparison with the G-SIMS spectra. The free web-based facility allows the library to grow rapidly as use by the community grows. Recent developments in G-SIMS including G-tip technology and the use of cluster ions will be discussed. Examples of the use of G-SIMS and SMILES to identify the structure for different molecules are provided as well as examples of how to use the web-based system.

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

[2] I. S. Gilmore and M. P. Seah, Appl. Surf. Sci., 231-232 (2004) 224.

[3] I. S. Gilmore, F. M. Green and M. P. Seah, Appl. Surf. Sci., 252 (2006) 6601.

[4] F.M. Green, E.A. Dell, I. S. Gilmore, M.P. Seah, Int J Mass Spectrom 272 (2008) 38

[5] SMILES, Daylight Chemical Information Systems, http://www.daylight.com/smiles/ .

8:40am **AS1-ThM3 Interrogating Surface Plasmons and Carbon Nanotubes with Four-Wave-Mixing Microscopy***, **E.O. Potma***, University of California, Irvine **INVITED**

Dual color four-wave-mixing is used to visualize the surface plasmon resonances of individual gold nanowires and the electronic excitations in single carbon nanotubes. The strong nonlinear signals, which are detected at the anti-Stokes frequency, originate from the electronic response of the nanostructures. In gold nanowires, the collective electron motions give rise to strong coherent anti-Stokes signals that can be used to study the orientation and relative strength of the nanostructure's plasmon resonances. In single-walled carbon nanotubes, coherent anti-Stokes contrast can be used to map the orientation and spatial delocalization of electronic excitations in individual nanotubes. Coherent anti-Stokes imaging of the material's electronic response allows for the first close-ups of the coherent nonlinear properties of individual nanostructures and molecules.

9:20am **AS1-ThM5 Observation of Ga^+ Focused Ion Beam Induced X-Rays (FIBIX)***, **L.A. Giannuzzi***, FEI Company*, B.P. Gorman*, Colorado School of Mines

Characteristic X-ray emission from a well grounded metal samples using standard 30 keV Ga^+ focused ion beams is demonstrated. X-ray yields are found to be on the order of 10^{-10} per incident ion, consistent with previous studies of low energy, high mass ion – solid interactions. X-ray yields were found to be highest for soft X-rays, i.e., low energy transitions or low atomic number target atoms. Bremstrahhlung X-ray emission was found to be minimal, possibly increasing the detectability limits compared with electron beam induced X-rays. The generation of heavy ion induced X-rays is consistent with a molecular-orbital level crossing model where velocity coupling between the primary ion beam and target atom electrons is not necessary and the majority of X-rays are in fact generated due to recoil effects within the ion – solid interaction cascade.

9:40am **AS1-ThM6 Advances in 2D and 3D TOF-SIMS Imaging of Organics by Means of a C_{60} Ion Microprobe and FIB Sectioning***, **G.L. Fisher***, Physical Electronics*, C. Szakal, G. Gillen,* National Institute of Standards and Technology*, S.R. Bryan*, Physical Electronics

An alternative approach for chemical imaging the interior of an organic specimen is to utilize FIB sectioning. Publications to date concerning FIB sectioning of organic specimens, e.g. simple biological structures, have been restricted to imaging the inorganic species by SEM-EDS. The union of FIB sectioning and TOF-SIMS analysis to achieve chemical imaging has been impeded by the difficulty of collecting secondary ions from the vertical FIB sidewall that is probed by a primary ion beam. Since the ultimate objective involves 3D reconstruction of successive 2D chemical images, it is highly advantageous to perform consecutive sectioning and analysis cycles without moving the sample. This constraint necessitates probing the vertical sidewall of the FIB-milled crater. Therefore, in order to image the vertical sidewall of a FIB-milled crater without moving (i.e. tilting) the sample, the TOF-SIMS analyzer must have as characteristics a large depth-of-field and a large solid angle-of-collection. In this presentation, new developments concerning the use of a C_{60} ion microprobe and FIB sectioning for advanced characterization of heterogeneous organic materials will be discussed. The advantages and challenges of joining FIB and TOF-SIMS will be demonstrated and discussed. Finally, we will discuss the application of cluster ion beams to recover the characteristic molecular signals within the FIB-milled area.

10:40am **AS1-ThM9 Temperature Studies on the Induced Molecular Desorption by Atomic and Cluster Projectiles**, ***D.A. Brenes***, *D.G. Willingham,* The Pennsylvania State University*, Z. Postawa,* Jagiellonian University, Poland*, N. Winograd*, The Pennsylvania State University

The temperature dependence in the molecular desorption of coronene films stimulated by 20-keV Au_1^+, Au_3^+, and C_{60}^+ projectiles were experimentally investigated by means of strong field laser photoionization coupled with time-of-flight secondary neutral mass spectrometry (ToF-SNMS) at 300 K and 77 K. The sputtering dynamics of highly energetic ion beams with surfaces have always been assumed to be temperature independent. However, recent data indicate this might not be the case for high energy cluster ion beams.

At 300 K, the kinetic energy distributions of ion beam desorbed coronene neutral molecules are projectile independent. The molecular desorption events stimulated by either projectile are ejected with a most probable translational energy of approximately 0.1 eV and show negligible differences in the high-energy component of the distribution when comparing the projectiles. However, at 77 K the most probable translational energy of ejection is shifted to higher energies as a result of cluster ion bombardment. A most probable translational energy of 0.5 eV is observed when using cluster projectiles such as 20-keV C_{60}^+. Fragments created by the C_{60} cluster ion sputtering dynamics are detected as low mass fragments at 300 K and exhibit a Maxwell-Boltzmann distribution. This behavior is not evident at 77 K or induced by the other projectiles.

In addition, by comparing the molecular to fragment ion (M/F) signal ratio of well known polyaromatic hydrocarbon photofragments, coronene molecules ejected by 20-keV Au_1^+ exhibit internal energies of sufficient magnitude to reach high energy fragmentation pathways resulting in photodissociation. Similarly, those that were desorbed by 20-keV C_{60}^+ not only have lower internal energies but the M/F signal ratios are enhanced at 77 K. This investigation suggests the desorption of coronene molecules by C_{60} primary ions is dependent on temperature and neutral molecules are ejected with low internal energies under cryogenic conditions.

11:00am **AS1-ThM10 Variation of Carbon Thickness on Magnetic Disk Media: Effects in TOF-SIMS Analysis on Metal Ion Attenuation and Lubricant Spectra**, ***A.M. Spool***, *R. Waltman, R. White*, Hitachi Global Storage Technologies, Inc.

This work continues a previous study[1] on thin overcoat effects on ion attenuation, and the change the proximity of the underlying metal layer has on the spectra of organic materials on top of the carbon. In this study, the overcoat thickness was varied over a larger range than in the previous study, down to bare metal. The samples were measured before and after application of a thin polymer film, a perfluoropolyether commonly used as a lubricant in the hard disk drive industry (Z-Tetraol). The spectra of the lubricant coated samples were explored both for the effect of the lubricant coating on the metal attenuation and for the effect of the varying carbon layer thickness on the lubricant spectra. For this series of samples, the total ion count is expected to vary from sample to sample as it reflects the differences between samples as much as relative individual ion intensities does. Also, the carbon itself produces little signal in TOF-SIMS spectra. The use of a system involving external standards will be described that allows the comparison of spectra from day to day without normalization.

1. Spool, A.; White, R., "Probing Thin Over Layers with Variable Energy / Cluster Ion Beams", Appl. Surf. Sci. Volume: 252 Issue: 19 (2006) 6517-6520

11:20am **AS1-ThM11 Large Area Combinatorial Near Edge X-ray Absorption Fine Structure Images: Parallel Process Determination of Molecular Bond Concentration and Orientation on Surfaces**, ***D.A. Fischer***, *C. Jaye,* National Institute of Standards and Technology*, P. Sobol, E.L. Principe,* E.L. Principe & Associates, LLC*, K. Scammon*, University of Central Florida

We show that simultaneous molecular orientation and bond chemistry of large area (18 mm x 13 mm) planar chemically heterogeneous surfaces can be obtained by combining near edge X-ray absorption fine structure (NEXAFS) spectroscopy, a new parallel process magnetic field electron yield optics detector, and a full field incident soft X-ray beam on the sample. The rapid parallel process magnetic field electron yield optics detector (LARIAT:Large ARea Imaging Analytical Tool) produces a series of two-dimensional NEXAFS spatial images as the incident soft X-ray energy is scanned above a K or L absorption edge. The image stack reveals information about the chemistry (including bond concentration) and orientation of the surface-bound molecules with 50-micron planar spatial resolution and sub-monolayer molecular sensitivity. The power of the combinatorial imaging NEXAFS method is illustrated by simultaneously probing the concentration and molecular orientation of single-strand DNA micro array sensors, semifluorinated molecular gradients, and organic electronic combinatorial device arrays. Other possible applications described include the surface orientation and chemistry of continuously graded polymer films and graded or patterned self-assembled monolayers that exhibit tunable surface properties of potential use in nanotechnology. We also envision combinatorial imaging NEXAFS as an insitu probe for catalyst discovery using micro arrays to directly image catalytic chemical activity of thousands of catalysts simultaneously under reaction conditions.

11:40am **AS1-ThM12 The Workfunction Modulation of Al/TiN Bilayer Metal Gate Electrode/High-k Dielectric Gate Stack for NMOS Application**, ***E.J. Jung***, *C.J. Yim, W.S. Im, C.Y. Kim, D.-H. Ko, M.-H. Cho*, Yonsei University, South Korea

In the selection of metal gate electrode material, workfunction is one of the important properties. However, the workfunction tunning of metal gate is more difficult than that of poly-Si gate electrode. The workfunction of poly-Si gate can be tuned by changing dopants and doping concentration, but the workfunction of metal gate shows fixed value because the workfunction of metal is its own characteristic. Thus many research groups have studied bilayer metal stacking methods for tuning interface workfunction between gate dielectric and electrode. In this work, we studied bilayer metal gate stack using Al/TiN bilayer for NMOSFET application, because Al and TiN are commonly used in conventional CMOS process. The high-k dielectric layer(HfO_2) and gate electrode stack is deposited by ALD and in-situ sputtering system, respectively. The thickness of Al/TiN bilayer was measured by TEM analysis. The workfunction of Al/TiN bilayer gate electrode/high-k dielectric gate stack is measured by backside XPS/UPS depth-profile method. This method is not influenced by gate dielectric type and oxide charge variation. The electrical properties are measured by C-V and I-V measurement methods.The workfunction value of Al/TiN bilayer gate stack was changed between workfunction of Al to workfunction of TiN depending on TiN layer thickness.

Applied Surface Science
Room: K - Session AS2+BI-ThM

Scanning Probe Studies of Biological Materials
Moderator: I.S. Gilmore, National Physical Laboratory, UK, S. Zauscher, Duke University

8:00am **AS2+BI-ThM1 Beyond the Optical Resolution in Living Cell: Biomedical Applications of Scanning Ion Conductance Microscopy**, *Y.E. Korchev,* Imperial College London, UK*,* ***S. Allen***, The University of Nottingham, UK **INVITED**

Molecular Biology has advanced we know much about the individual molecular components that make up living cells down to the level of the individual atoms. The challenge, however, is to fully understand the functional integration of these components. This requires determining how the molecular machines that make up a living cell are organized and interact together not at the atomic length scale but on a nm scale. To do this we need to develop and applying nanoscale techniques for the visualisation and quantification of cell machinery in real-time and on living cells. This will lead to detailed, quantitative models of sub-cellular structures and molecular complexes under different conditions for both normal and diseased cells. This approach ultimately requires the development of novel biophysical methods. We have recently pioneered the development of an array of new and powerful biophysical tools based on Scanning Ion Conductance Microscopy that allow quantitative measurements and non-invasive functional imaging of single protein molecules in living cells. Scanning ion conductance microscopy and a battery of associated innovative methods are unique among current imaging techniques, not only in spatial resolution of living and functioning cells, but also in the rich combination of imaging with other functional and dynamical interrogation methods. These methods, crucially, will facilitate the study of integrated nano-behaviour in living cells in health and disease.

8:40am **AS2+BI-ThM3 Nanometer Scale Patterning of Biomolecules using Near-Field Optical Methods**, ***G.J. Leggett***, University of Sheffield, UK

The integration of top-down (lithographic) and bottom-up (synthetic) methods remains one of the outstanding challenges in molecular nanoscience. There are no established tools for the manipulation of surface chemical structure in the length range from ca. 100 nm to the dimensions of a single biomacromolecule. Scanning near-field photolithography (SNP), in which a scanning near-field optical microscope coupled to a UV laser is employed as a light source, may be used to execute specific molecular transformations with a spatial resolution of a few tens of nm and, at best, 9 nm (ca. λ/30). Several strategies will be described for the patterning of proteins and nucleic acids on metal and oxide surfaces. We demonstrate two approaches. First, photodegradation of oligo(ethylene glycol) (OEG) functionalised surfaces provides a simple route to the covalent attachment of proteins to non-fouling surfaces. Photodegradation of OEG-terminated thiols provides a simple, one-step route to the conversion of a protein-resistant surface to a protein-binding one. Similar methodologies may be extended to oxide surfaces, through the formation of OEG-functionalised siloxane films. Photodegradation yields aldehyde functionalities, to which nitrilo triacetic acid (NTA) functionalised amines may be coupled, and subsequently dertivatised, following nickel complexation, with histidine-tagged proteins, providing a facile route to the site-specific immobilisation of proteins on glass. Second, siloxane monolayers offer fruitful opportunities for the incorporation of synthetic chemical methods into nanolithography. Halogenated monolayers may be converted to aldehydes or to carboxylic acids, by controlling the exposure. Alternatively, 2-nitrophenylpropyloxycarbonyl (NPPOC) protected aminosiloxane monolayers on glass may be selectively deprotected by SNP, yielding amine groups for further functionalisation with very high spatial resolution. The synthetic flexibility and versatility of photochemical methods, when combined with near-field methods for control of exposure, offers enormous potential for integrating top-down and bottom-up methods.

9:00am **AS2+BI-ThM4 Nanomechanics of Glycopeptide Resistant Superbugs and Superdrugs**, ***J. Ndieyira,*** Uni. College London, UK and Jomo Kenyatta Univ. of Agriculture and Tech., Kenya*, A. Donoso Barrera, M. Vogtli,* Uni. College London, UK*, M. Sushko,* Uni. College London, UK and PNNL*, D. Zhou,* Univ. of Leeds, UK*, M. Cooper,* The Univ. of Queensland, Australia*, C. Abell,* Univ. of Cambridge, UK*, T. Strunz, G. Aeppli, R. McKendry*, Uni. College London, UK

The discovery of penicillin in 1928 marked the beginning of a remarkable new era of antibiotic 'wonder drugs', saving millions of lives across the world. However the widespread and often indiscriminate use of antibiotics has fuelled the alarming growth of antibiotic resistant superbugs, including methicillin resistant Staphylococcus aureus (MRSA) and vancomycin resistant Enterococci (VRE). To remain one step ahead of the superbugs, there is now an urgent need to develop new antibiotics and yet the drug pipeline is severely limited. We recently reported the nanomechanical detection of vancomycin-cell wall peptide interactions on cantilever arrays and discriminated between vancomycin-sensitive and vancomycin-resistant phenotypes.[1] In this talk I will present our new work which exploits this technology for the search of new superdrugs active against VRE. We have investigated a series of vancomycin derivatives and detect a dramatic enhancement in surface binding affinities compared to homogeneous solution measurements. We identify a glycopeptide which binds 11,000 more strongly to resistant peptide analogues. Our findings reveal fundamental new insights into the mechanism of antibiotic bindings to a model bacterial cell wall peptides using nanosensors, which not only has important implications on the design of new devices with significantly improved antibiotic detection sensitivity but will also impact on our understanding of the mode of action of antibiotics on intact bacteria. These findings highlight the potential of BioMEMs devices for application in pharmaceutical industry and will accelerate the discovery of new antibiotics.

[1] 'Nanomechanical detection of antibiotic mucopeptide binding in a model for superbug drug resistance.' Ndieyira, W.N, Watari, M., Donoso-Barrera, A., Batchelor, M., Zhou, D., Vogtli, M., Bactchelor, M., Cooper, M., Strunz, T., Abell, C.A., Rayment, T., Aeppli, G. & McKendry R.A. *Nature Nanotechnology* **3**, 691 - 696 (2008). Also featured in Nature Nanotechnology News and Views, BBC, New Scientist, Physics Today, Chemistry World, UK T&I.

9:20am **AS2+BI-ThM5 Single Biomolecule Force Spectroscopy Measurements; the Importance of Controlled Surface Chemistry***, S. Allen,* The University of Nottingham, UK*,* ***S. Zauscher***, Duke University

Over the past decade, considerable interest has focussed on the ability of atomic force microscopy (AFM) and related techniques to record forces on or between single biological molecules. Many elegant examples are evident within the literature where such approaches have been employed, for example, for studies of force induced protein and RNA unfolding processes, and the dissociation of a wide-range of biomolecular complexes, including those involved in cell adhesion. Despite these elegant examples, and the considerable advantages of performing measurements at the single molecule level, such measurements are still far from routine. Indeed, even in the most experienced hands the experiments can suffer various problems which can arise from poor control of the chemistries employed for biomolecular surface attachment e.g. such as non-specific binding, difficulties in single molecule pickup and variability between experiments.

This presentation will provide an overview of the approaches we have employed in recent studies to address such issues. This for example, will include our studies of the mechanical properties of long molecules of DNA (>1000 base pairs) in which we have demonstrated the advantages of the addition specific terminal functionalities for surface attachment [1]. The advantages will be highlighted through our investigations of the effects on DNA mechanical properties of a range of different DNA binding molecules (e.g. drugs and proteins involved in DNA replication [1,2]). For studies of the dissociation of biomolecular complexes, we will highlight the advantages of an alternative approach, in which we have exploited the unique properties of dendron functionalized surfaces. Developed in collaboration with the group of Professor J.W. Park (Pohang University of Science and Technology (POSTECH), we have recently employed such surfaces for studies of DNA hybridization [3], and interactions between intracellular signal transduction proteins [4].

[1] W. Zhang, R. Barbagallo, C. Madden, C.J. Roberts, A. Woolford, S. Allen. (2005) *Nanotechnology* 16 2325-2333

[2] W. Zhang, C. Machon, A. Orta, N. Phillips, C.J. Roberts, S. Allen, P. Soultanas (2008) *Journal of Molecular Biology* 377, 706-714

[3] J. Yung, B.J. Hong, W. Zhang, S.J.B. Tendler, P.M. Williams, S. Allen and J.W. Park (2007). *Journal of the American Chemical Society*, 129(30), 9349-9355.

[4] I.H. Kim, H.Y. Lee, H.D. Lee, Y.J. Jung, S.J.B. Tendler, P.M. Williams, S. Allen, S.H. Ryu, and J.W. Park (2009) *Analytical Chemistry* 81(9), 3276-3284

9:40am **AS2+BI-ThM6 Nanoarrayed Biomolecular Recognition followed by AFM**, ***P. Lisboa****, L. Sirghi, A. Valsesia, P. Colpo, F. Rossi*, JRC-European Commission, Italy

The use of nanoarrayed surfaces in the field of biomolecular recognition is very promising for the improvement of bio-detection performance. Atomic Force microscope (AFM) is widely used to produce and characterize nanoarrayed surfaces and to carry out studies in the biological field. This work presents the study and characterization by AFM measurements of the fabrication steps of nanoarrayed surfaces based on organothiols (carboxylic and Polyethylene oxide) and the study of an immunoassay performed on these surfaces. The immunoassay was based on the bio-recognition between Human IgG/anti-Human IgG.

The nanoarray was fabricated by plasma colloidal lithography following the procedure developed in our lab. AFM studies of the process of nanoarray fabrication showed that during lithographic process, the etching step is crucial for the final the characteristics of the surface and that the process originates a good chemical nano-contrast.

The AFM analysis of the bio-interaction was performed after Human IgG immobilisation and anti-Human IgG recognition steps. The nanoarray was incubated with Human IgG solution resulting in an increase of height on the nano areas. The AFM image demonstrates that IgG molecules are adsorbed mainly on the border between the two organothiols. The preferential disposition of proteins on the borders of the two different materials with hydrophobic and hydrophilic groups was already reported and associated to the fact that the proteins tend to adsorb where they can find better accommodation. In our case, this effect can be explained by the fact that having the carboxylic spots with hydrophilic character the IgG hydrophobic groups are better accommodated on the border between the two materials, leading to higher adsorption on the boundaries. After the Human IgG incubation, the surface was blocked with BSA and the following step consisted in the immobilisation of anti-Human IgG. After this step, a height increase on the border of the COOH nano area is detected by AFM. The increase is about the double of the initial with Human IgG. This is an indication that the anti Human IgG binds specifically with the Human IgG already on the surface. The distribution on the borders of the nano-area can explain the better efficiency of the nano-patterns in biomolecular recognition as already described on different studies. The preferential proteins immobilisation on the nano areas boundaries seems to improve the binding efficiency of the immobilised Human IgG bio-detector by a better availability of the binding sites on the surface and reduction of steric hindrance.

10:40am **AS2+BI-ThM9 Deciphering Nanoscale Interactions: Artificial Neural Networks and Scanning Probe Microscopy***, S. Jesse, M.P. Nikiforov, O. Ovchinnikov,* ***S.V. Kalinin***, Oak Ridge National Laboratory

Scanning Probe Microscopy techniques provide a wealth of information on nanoscale interactions. The rapid emergence of spectroscopic imaging techniques in which the response to local force, bias, or temperature is measured at each spatial location necessitates the development of data interpretation and visualization techniques for 3- or higher dimensional data sets.

In this presentation, we summarize recent advances in applications of neural network based artificial intelligence methods in scanning probe microscopy. The examples will include biological identification based on the dynamic of the electromechanical response, direct mapping of dynamic disorder in ferroelectric relaxors, and reconstruction of random bond-random field Ising model parameters in ferroelectric capacitors. The future prospects for smart multispectral SPMs are discussed.

Research was supported by the U.S. Department of Energy Office of Basic Energy Sciences Division of Scientific User Facilities and was performed at Oak Ridge National Laboratory which is operated by UT-Battelle, LLC.

11:00am **AS2+BI-ThM10 Scanning Probe and Differential Interference Contrast Imaging Methods for Studying Adhesion-Induced Tension and Membrane Fluctuation of Red Blood Cells**, ***N. Farkas***, *H. Kang*, National Institute of Standards and Technology, *F. Tokumasu,* NIAID, NIH, *J. Hwang, J.A. Dagata*, National Institute of Standards and Technology

Red blood cell (RBC) membrane fluctuation mediated by cooperative relationship between its cytoskeleton and lipid bilayer plays an important role in protein dynamics that is indicative of structural-functional properties of healthy or diseased RBCs. Probing of this characteristic membrane behavior requires dynamic interrogation of RBCs under physiological conditions by high-resolution, noninvasive microscopy techniques for which RBCs are required to be immobilized on a substrate while maintaining their viability. Therefore, detailed understanding of the adhesion process and its consequence on RBC shape and dynamic membrane response is critical. In the present study, we demonstrate our ability to engineer substrates with tunable surface zeta potential (SZP) for precise control of RBC adhesion. Specifically, 10 nm gold nanoparticles are adsorbed on poly-L-lysine coated cover slips as a compliant layer to locally modify the non-specific interaction between RBC membrane and substrate. By combining scanning probe microscope (SPM) and differential interference contrast (DIC) imaging techniques we develop a quantitative measurement methodology to investigate the relationship between attachment strength, RBC morphology, cell vibration and membrane fluctuation on these charge and topographically modulated substrates. Adhesion-induced tensing of the RBC membrane on modified substrates leads to changes in cell shape and functionality as determined by SPM force-volume and DIC monitoring of membrane dynamics. The substrate preparation and measurement methods presented here provide a feasible platform to obtain structure-function relationships of viable RBCs under physiological conditions and with that allow us to investigate dynamic behavior of RBCs and their response to diseases.

11:20am **AS2+BI-ThM11 Effect of Different Cations on the Nanomechanical Response of a Model Phospholipid Membrane : A Force Spectroscopy Study**, ***L. Redondo-Morata***, *G. Oncins, F. Sanz*, University of Barcelona, Spain

Understanding the effect of mechanical stress on biological membranes is of fundamental importance in biology since cells are known to naturally perform their function under the effect of a complex combination of forces. The chemical composition of such membranes is the ultimate responsible for determining the cellular scaffold, closely related to its function. Nevertheless, there is another factor that has been widely discussed in theoretical works but never experimentally tested in an accurate way, which is the presence of ions and their nature (radius and charge) on the stability of the bilayers. Micro-scale assays have revealed a wealth of information regarding the overall membrane mechanical resistance. Nonetheless, the diversity in the chemical composition of such membranes makes it difficult to individually probe the mechanical contribution of every particular membrane component. Here we use force spectroscopy to quantitatively characterize the nanomechanical resistance of supported lipid bilayers as a function of ionic strength and the composition of the electrolyte thanks to a reliable molecular fingerprint that reveals itself as a repetitive jump in the approaching force curve, hallmark of bilayer rupture. By systematically testing a set of bilayers composed of different phospholipids immersed in electrolytes composed of a variety of monovalent and divalent cations, we first show that the cationic radius, its charge density and the hydration number have an independent and important contribution to the overall bilayer mechanical stability. This work opens up avenues for characterizing the membrane (nano)mechanical stability and to assess the effect of different ions in the structure of the bilayers in an experimental and reproducible way.

Electronic Materials and Processing
Room: B1 - Session EM-ThM

Oxide Semiconductors
Moderator: S.M. Durbin, University of Canterbury, New Zealand

8:20am **EM-ThM2 Defect States in the Wide Gap Semiconducting Oxide Ga_2O_3**, ***T.C. Lovejoy***, *S. Zheng,* University of Washington*, E.G. Villora, K. Shimamura,* National Institute for Materials Science, Japan*, F.S. Ohuchi, M.A. Olmstead*, University of Washington

Ga_2O_3 is a transparent wide gap semiconducting oxide with potential applications as a transparent conductive oxide (TCO) or phase change memory (PCM) materials system. The mechanism for conductivity in this material is still under debate. The long established picture involves conduction by oxygen vacancy defect states, but unintentional silicon doping may also contribute. A recent paper [Appl. Phys. Lett. 92 202120 (2008)] shows the conductivity can be intentionally controlled over three orders of magnitude by silicon doping on the order of typical Si impurity levels in Ga_2O_3 source materials. In light of this, the actual role of oxygen vacancies is unclear. We illuminate this issue by studying separately the contribution to the electronic density of states of single crystal β-Ga_2O_3 by intentional silicon doping and oxygen deficiency with X-ray photoemission spectroscopy (XPS). Ar^+ ion sputtering is an effective means of reduction that causes states to appear above the valence band maximum, which disappear on subsequent annealing. We demonstrate qualitative agreement with previously published density functional theory results [Nature Materials 7 391 (2008)] on the effect of oxygen deficiency in Ga_2O_3. Forthcoming hard x-ray photoemission and transport measurements will further elucidate this issue.

8:40am **EM-ThM3 Trends in Surface Electronic Properties of Oxide Semiconductors**, ***T.D. Veal***, *P.D.C. King, C.F. McConville*, University of Warwick, UK **INVITED**

Oxide semiconductors have enormous potential for new and innovative uses and may also improve existing device applications. However, the fundamental properties of some of the oxide semiconductors (such as In_2O_3, Ga_2O_3 and CdO) remain either controversial or largely unknown. The semiconducting oxides have traditionally been grown using low cost, low quality techniques, such as sputtering, resulting in poor microstructure material with high levels of impurities and defects. The fact that some of these materials in their low quality form have seen significant industrial use as transparent conductors has perhaps contributed to the belated recognition of their possibilities as semiconductors in their purer form. Relatively recently, with the advent of high-purity oxide semiconductor films by high-quality growth methods, such as molecular-beam epitaxy and metal-organic vapor phase epitaxy, the fundamental properties have begun to emerge and the material characteristics have been vastly improved. Here the surface and bulk electronic properties of several such high-quality oxide semiconductors (In_2O_3, CdO, $SrTiO_3$, ZnO and SnO_2) will be reported. Optical, electrical and structural properties of the semiconducting oxide films will be presented, including data on the revision of the band gap of In_2O_3 from 3.7 eV to less than 3.0 eV [1]. Both the valence band density of states and the surface electronic properties of the oxide semiconductors have been studied using high-resoultion photoemission spectroscopy [1,2]. A common property of the materials with a high size and electronegativity mismatch between the cation and oxygen atoms is found to be the presence of a surface electron accumulation layer [3,4] which is in marked contrast to the electron depletion generally observed at the surface of conventional compound semiconductors. The origin of this phenomenon will be discussed in terms of the band structure of the semiconducting oxides. The five groups where the samples were grown are gratefully acknowledged.

[1] P. D. C. King, T. D. Veal, F. Fuchs, Ch. Y. Wang, D. J. Payne, A. Bourlange, H. Zhang,

G. R. Bell, V. Cimalla, O. Ambacher, R. G. Egdell, F. Bechstedt, and C. F. McConville,

Phys. Rev. B 79 (2009) in press.

[2] P. D. C. King, T. D. Veal, A. Schleife, J. Zúñiga-Pérez, B. Martel, P. H. Jefferson, F. Fuchs,

V. Muñoz-Sanjosé, F. Bechstedt, and C. F. McConville, Phys. Rev. B 79 (2009) 205205.

[3] P. D. C. King, T. D. Veal, D. J. Payne, A. Bourlange, R. G. Egdell, C. F. McConville,

Phys. Rev. Lett, 101 (2008) 116808.

[4] P. D. C. King, T. D. Veal, P. H. Jefferson, J. Zúñiga-Pérez, V. Muñoz-Sanjosé, and

C. F. McConville, Phys. Rev. B 79 (2009) 035203.

9:20am **EM-ThM5 STM and XPS studies of ITO (001) Surfaces**

H. Morales, *U. Diebold*, Tulane University

Tin-doped Indium Oxide (ITO) is a transparent conducting oxide and extensively used in flat panel displays, solar cells, and organic-light-emitting-diodes. Despite the industrial significance and versatility of this material, little is known about its surface structure.

Epitaxial In_2O_3 (001) thin films with a Sn content between 0 and 30 at% were grown on Yttria stabilized Zirconia YSZ (001) using oxygen-plasma-assisted molecular beam epitaxy (MBE). The growth was monitored with Reflection-high-energy-electron-diffraction (RHEED). Low-energy-electron-diffraction (LEED) showed well ordered surfaces.

Angle-resolved X-ray photoemission (ARXPS) performed *in situ* shows that Sn^{4+} substitutes In^{3+} in the In_2O_3 bixbyite lattice and Sn enrichment in the near-surface region. A shoulder at the *Sn* $3d_{5/2}$ peak at off-normal-emission angles indicates a Sn^{2+} oxidation state. The *O 1s* peak shows significant asymmetry in In_2O_3 and a more symmetric peak shape with increasing Sn content. This indicates that the charge imbalance, produced by substituting Sn^{4+} for In^{3+} in the In_2O_3 lattice, is compensated by introducing extra oxygen in the bixbyite structure.

Preparing a flat ITO (001) surface is challenging due to its polar character. A Sn concentration of more than 15 at% is necessary to stabilize ITO (001). Empty-states Scanning Tunneling Microscopy (STM) shows terraces 100 to 400nm^2 in size and an overall surface roughness of 0.5nm. In agreement with previous theoretical work we find that the ITO (001) surface is oxygen terminated. Features in atomically-resolved STM images are interpreted with a model involving dimerization of surface oxygen.

9:40am **EM-ThM6 Cyclic In-Situ Deposition and Etching for Growth of High-Quality Zinc Oxide by Metalorganic Chemical Vapor Deposition**

E.J. Adles, *D.E. Aspnes*, NC State University

Zinc oxide (ZnO) is a transparent conducting oxide with a room-temperature band gap of 3.37 eV. It is currently under investigation for magneto-optic applications and as a cheap alternative for optic and optoelectronic devices currently depending on gallium and indium. While epitaxial ZnO can be grown by a number of laboratory-scale methods, growth by industrial-scale processes such as metalorganic chemical vapor deposition (MOCVD) is hampered by particulate ZnO formed in the gas phase and by the natural tendency of ZnO to deposit in multiple orientations. Both prevent deposition of high-quality epitaxial material. After careful consideration of gas-phase chemistry and our real-time polarimetric data, we have developed a cyclic MOCVD growth process based entirely on diethylzinc where conditions are alternated between brief periods of deposition and etching. The gas-phase particles are used as the source of ZnO. The etching part of the cycle preferentially removes unwanted orientations, since these typically have higher free energies. The result is dense two-dimensional epitaxial ZnO. Because etching is driven chemically instead of thermally, infilling and smoothing occur at much lower temperatures and shorter time scales than previously discussed in the literature.

10:40am **EM-ThM9 Formation of Zn Nanoparticles on Single Crystal ZnO Surfaces with Ultraviolet Laser Irradiation**

E. Kahn, *S. Langford*, *T. Dickinson*, Washington State University

Many dielectric crystals color in the visible region of the spectrum under intense ultraviolet light such as excimer laser irradiation. We have shown previously that in many cases these are due to electron hole pair production via two photon absorption. Examples are coloration of alkali halides and alkaline earth halides where self=trapped excitons lead to formation of strongly absorbing defects. Recently we were surprised to see dramatic coloration of single crystal ZnO, a wide bandgap (3.37 eV) semiconductor of significant technological interest, under exposure to 193 nm ArF excimer laser radiation. The increase in absorption is very broadband, extending from the bandgap into the infrared, appearing as near black to grey. We present careful measurements of the properties of this coloration and determine its origin. We present convincing evidence that it is due to the formation of zinc metal nanoparticles residing on the surface of the irradiated region. This evidence involves AES, TEM, XRD, UV-VIS reflection and absorption spectroscopy as well as Positron Annihilation Spectroscopy. As expected, laser fluence has considerable impact on the size, number, and spatial distribution of these nanoparticles. We present a model for the production of this Zn metal rich surface and discuss applications including plasmonics. Related optical property measurement will be presented. Furthermore, we show that with suitable choices of laser exposure we are able to convert the originally n-type ZnO to p-type. We are carrying out additional experiments to confirm that this transformation is dependent on the formation of O-vacancies. Supportive UHV mass spectroscopy measurements of the emitted particles during laser exposure show copious release of atomic and molecular oxygen suggesting O depletion is occurring.

This work was supported by the U.S. Department of Energy, DE-FG02-04ER-15618

11:00am **EM-ThM10 Preparation of N-doped p-type ZnO Film by Metal-Organic Chemical Vapor Deposition**

W. Chen, *Y. Chen*, *J. Liang*, *C. Lu*, National Dong Hwa University, Taiwan

ZnO is a promising material used in short-wave optoelectronic devices such as light emitting diodes. However, one important issue that should be resolved beforehand is the fabrication of p-type ZnO film, which is difficult due to various intrinsic donor defects inside ZnO crystals such as zinc interstitials or oxygen vacancies. Nitrogen (N) has been considered to be an effective acceptor dopant to realize p-type ZnO. In this work, we prepared N-doped p-type zinc oxide thin films deposited on sapphire by metal organic chemical vapor deposition. We have successfully prepared high quality p-type ZnO film by changing VI/II ratio (O_2 / DMZn flow ratio), and the p-type ZnO film can be fabricated reproducibility using this method. Dimethylzinc (DMZn) and N_2O were used as zinc precursor and N dopant source. The growth temperature was in the range of 300-400°C and the chamber pressure was 100 Torr. The O_2 flow rate is in the range 900-1100 sccm and DMZn carrier gas flow rate is in the range 2-10 sccm. We found ZnO film prepared using N_2O only as O source show n-type. After 800°C under O_2 ambient annealing for 1 hr, a few sample originally n-type became p-type. The p-type concentration is $1.4x10^{18}$ cm^{-3}. XRD shows higher ZnO (002) peak intensity of the film after annealing than that before annealing. On the other hand, if we use O_2 and N_2O together as O source during ZnO growth, most films show p-type even before annealing. XRD spectrum and PL analysis suggest that appropriate oxygen flows can improve the quality of ZnO film to eliminate those excessive donor defects. Hall measurement shows that the resistance is 0.24 Ωcm and its corresponding hole concentration is $7.16x10^{18}$ cm^{-3}. The N 1*s* peak in XPS spectra is located at 398.5 eV, which represent N–Zn bonds. The N–Zn bonds imply that N is located at O position in ZnO crystal and forms bond with Zn. N_O is known as an acceptor defect in the ZnO film, so the presence of N-Zn bonds suggest the acceptor formation in the ZnO film. Since N_2O is the only source for N, the formation of N–Zn bond suggests that using N_2O in the process is helpful in p-type formation of ZnO films.

11:20am **EM-ThM11 Growth of Ga-doped ZnO Thin Film Prepared by MOCVD for TCO Application**

K. Chou, ***J. Liang***, *Y. Chen*, *C. Yang*, National Dong Hwa University, Taiwan

The group-III elements, such as Al, Ga and In, are possible dopants for ZnO to improve the electric conductivity of ZnO thin film. Since Ga has lower cost than In and has higher oxidation resistance than Al, it becomes the preferred dopants for ZnO thin film for transparent conducting oxide (TCO) application. In the research, we used MOCVD method with Ga doping to prepare the Ga-doped ZnO thin film (GZO) on the corning-1737 glass substrate. We changed the amount of Ga doping into ZnO thin films to increase the carrier concentration and decrease the electric resistivity of ZnO thin film. We used dimethylzinc (DMZn) and oxygen as Zn and O sources, respectively, and kept both of them constant. The trimethylgallium (TMGa) was used as Ga source, and the Ga/Zn was controlled in the range of 0.8% to 2.8% by adjusting TMGa flow rate. From the top views of GZO thin films, we observed that there are small grains arranged loosely on the surface of the undoped ZnO thin film. After doping Ga into ZnO thin films the grains become bigger, and the arrangement of grains becomes compact. However, when the Ga/Zn flow ratio is over 1.6%, the grains of the GZO thin film become small again. The variation trend of grain size observed by SEM is similar with the results of FWHM in XRD spectra. The FWHM decreases as Ga/Zn flow ratio increases to 1.6%, but then the FWHM increases as Ga/Zn flow ratio increases from 1.6% to 2.8%. It implies the crystallinity of GZO thin films was improved with the Ga/Zn flow ratio and has the best crystallinity at 1.6% of the Ga/Zn flow ratio. Afterwards the crystallinity of GZO thin film worsens when the Ga/Zn ratio increases from 1.6% to 2.8%. The Hall measurement shows the electrical resistivity decreases with increasing Ga/Zn flow ratio, and the carrier concentration increases with Ga/Zn flow ratio. In addition, we found the mobility is still about 29 cm^2/Vs even as the carrier concentration has the highest value around 7.1×10^{19} cm^{-3}. It reveals that the Ga doping can significant improve the conductivity and increase the carrier concentration. Since the site which the Ga occupies in ZnO thin films can influence the electric behavior and the structure, we will use XPS to determine the Ga bond for determining the site of Ga occupied. Because the transparency is an important factor for TCO application, we will also show the transparency of GZO by the transmission spectra.

11:40am **EM-ThM12 Preparation of p-type ZnO by Codoping Method using Gallium and Arsenic**, ***H. Jen***, *Y. Chen, M.S. Wong, H. Kuo*, National Dong Hwa University, Taiwan

In this research, we successfully prepared p-type ZnO films by rapid thermal annealing (RTA) of Ga and As codoped ZnO films deposited by magnetron DC sputtering using target made of ZnO mixed with Ga_2O_3 and Zn_3As_2 powders. These codoped p-type ZnO films were deposited on undoped silicon substrates at 300ºC and have hole concentrations of 10^{18}~ 10^{19} cm^{-3} and resistivities of 10^{-1}~10^{-2} ohm-cm. We changed the oxygen flow rate from 0 to 50 sccm and the RTA time for 30 seconds, 2 minutes, and 5 minutes. From the Hall measurement, the electrical conduction type of codoped ZnO film converted from n-type to p-type after RTA of the films at 1000ºC for 30 seconds. But it converted to n-type conduction again for longer annealing time of 2 minutes and 5 minutes. The X-ray diffraction (XRD) data indicates the crystallinity of the codoped films is improved by increased RTA time. From the field emission scanning electronic microscopy (FESEM) observation, we found the grain size of ZnO increases with annealing time, but there is less significant change of grain size after 30 seconds of RTA. The result indicates the grain boundary may not affect the electrical conduction type. According to the room temperature photoluminescence (PL) spectra, we found that the sample prepared with oxygen flow rate of 30 sccm followed by RTA at 1000ºC for 30 seconds in O_2 ambient had the highest near band edge (NBE) emission intensity. It indicates this RTA condition is the optimum RTA condition among other conditions. We found that the p-type ZnO films can be obtained with the same RTA parameter even though the ZnO films are prepared with different oxygen flow rate during deposition, i.e., the p-type conduction is independent of the oxygen flow rate in the deposition process and the ZnO films need an RTA process to activate the p-type conduction. From the X-ray photoelectron spectroscopy (XPS), we can not find the Ga-As bonding either in Ga 3d peak or As 3d peak. It indicates the Ga and As do not bond together in the ZnO film. This fact agrees with the codoping theory proposed by Yamamoto and Katayama-Yoshida. According to others researches and calculations, doped p-type ZnO films are produced in the oxygen-rich growth condition. We think the codoping method, which can lower the Madelung energy and activate the deep acceptor state may enhance p-type formation. Thus even in the zinc-rich condition, we can still obtain p-type ZnO thin films at appropriate RTA condition by codoping method.

Inkjet Technology: Printing, Materials Processing, and Microfluidics Fundamentals Topical Conference
Room: B3 - Session IJ+BI+MN+SE+AS-ThM

Inkjet Technology: Novel and Emerging Applications
Moderator: C. Klapperich, Boston University

8:00am **IJ+BI+MN+SE+AS-ThM1 An Overview of the Use of Ink-jet Technology for Non-traditional and Emerging Applications**, ***D.B. Wallace***, MicroFab Technologies, Inc. **INVITED**

In the last decade ink-jet printing technology has come to be viewed as a precision microdispensing tool. Today, this tool is being used in a wide range of manufacturing and instrument applications. Manufacturing applications include electrical (solders & nanometal conductors) & optical (microlenses & waveguides) interconnects; sensors (polymers & biologicals); medical diagnostic tests (DNA, proteins, cells); drug delivery (microspheres, patches, stents); scaffolds for tissue engineering; nanostructure materials deposition; and MEMS (Micro-Electrical-Mechanical) devices and packaging. Instrument applications using ink-jet technology have received less notice than manufacturing applications, but represent a growing class. Applications include protein identification (peptide mass fingerprinting, ion mass spectrometry tissue imaging) and structure analysis (protein crystallization); laser surgery and machining; medical diagnostic instruments; extreme ultra-violet (EUV) radiation generation; and explosive detector calibration. This paper illustrates some of the manufacturing and instrument applications of ink-jet technology.

8:40am **IJ+BI+MN+SE+AS-ThM3 Inkjet Printing for Bioengineering Applications**, ***T. Boland***, Clemson University **INVITED**

We will present the inkjeting of bioink, which may include active compounds such as drugs and living cells as well as non-active, scaffolding materials to build two- and three-dimensional constructs for medical treatment. The technology faces several limitations that present interesting engineering opportunities. The nature and scope of the problems will be discussed in the context of the fabrication of microvasculature. The current tissue-engineering paradigm is that successfully engineered thick tissues must include vasculature. As biological approaches alone such as VGEF have fallen short of their promises, one may look for an engineering approach to build microvasculature. Layer-by-layer approach for customized fabrication of cell/scaffold constructs have shown some potential in building complex 3D structures. With the advent of cell printing, one may be able to build precise human microvasculature with suitable bioink. Human Microvascular Endothelial Cells (HMEC) and fibrin were studied as bioink for microvasculature construction. Endothelial cells are the only cells to compose the human capillaries and also the major cells of blood vessel intima layer. Fibrin has been already widely recognized as tissue engineering scaffold for vasculature and other cells, including skeleton/smooth muscle cells and chondrocytes. In the study presented here, we precisely fabricated micron-sized fibrin channels using a drop-on-demand polymerization. This printing technique uses aqueous processes that have been shown to induce little, if any, damage to cells. When printing HMEC cells in conjunction with the fibrin, we found the cells aligned themselves inside the channels and proliferated to form confluent linings. Current studies to characterize the biology and functionality of these engineered microvascular structures will be presented. These data suggests that a combined simultaneous cell and scaffold printing can promote HMEC proliferation and microvasculature formation.

9:20am **IJ+BI+MN+SE+AS-ThM5 Inkjet Printing for MEMS Fabrication**, ***J.A. Kubby***, *O. Azucena,* University of California, Santa Cruz, *C.L. Goldsmith, D. Scarbrough,* MEMTronics Corporation, *A.S. Mangalam*, Tao of Systems Integration, Inc. **INVITED**

In this presentation we will review the use of inkjet printing to fabricate Micro-Electro-Mechanical Systems (MEMS). We are investigating the use of sintered silver nanoparticle inks for the structural layer and polymers for the sacrificial layer in printed MEMS fabrication. As an example, inkjet printing technology has been used to fabricate microwave transmission lines for an RF MEMS switch on a glass substrate (with MEMTronics Corporation). 50 mm resolution was obtained using 10 pL drop volumes on a Corning 7740 glass substrate. The conductivity of the sintered silver structures were 1/6 that of bulk silver after sintering at a temperature much lower than the melting point of bulk silver. A comparison of the DC resistance of the sintered silver shows that it can match the performance for electroplated and etched copper. Printed coplanar lines demonstrated losses of 1.62 dB/cm at 10 GHZ and 2.65 dB/cm at 20 GHz. We will also discuss printing MEMS hot-wire anemometer sensors for use in aeronautical applications (with Tao of Systems Integration).

10:40am **IJ+BI+MN+SE+AS-ThM9 Formation and Surface Characterisation of a Combinatorial Acrylate Polymer Microarray Produced by an Ink-Jet Printer**, ***A.L. Hook***, *J. Yang,* University of Nottingham, UK, *D.G. Anderson, R.S. Langer,* Massachusetts Institute of Technology, *M.C. Davies, M.R. Alexander*, University of Nottingham, UK

Polymer microarrays are emerging as a key enabling technology for the discovery of new biomaterials. This platform can readily be screened for properties of interest and for correlating surface chemistry with biological phenomenon. A method for forming polymer microarrays has been developed whereupon a contact printer is used to deposit nanolitre volumes of premixed acrylate monomer and initiator to defined locations of a glass slide with subsequent UV irradiation[1]. This results in polymerisation occurring on the slide, offering a useful high throughput materials discovery platform. The identification of relationships between cell response to these materials and surface properties is facilitated by high throughput analysis of this slide format[2,3]. Here, we have formed these polymer microarrays for the first time using ink-jet printing, to offer flexibility of slide production. Characterisation was achieved using a high throughput surface analysis approach, including the techniques of X-ray photoelectron spectroscopy, time-of-flight secondary ion mass spectroscopy and sessile drop water contact angle measurements[2]. Of particular interest were polymers containing ethylene glycol functionality that were investigated for their switchable properties under biologically relevant conditions.

[1] D. G. Anderson, S. Levenberg, R. Langer, *Nat.Biotechnol.* **2004**, *22*(7), 863.

[2] A. J. Urquhart, D. G. Anderson, M. Taylor, M. R. Alexander, R. Langer, M. C. Davies, *Adv.Mater.* **2007**, *19*(18), 2486.

[3] Y. Mei, S. Gerecht, M. Taylor, A. J. Urquhart, S. R. Bogatyrev, S. W. Cho, M. C. Davies, M. R. Alexander, R. S. Langer, D. G. Anderson, *Adv. Mater.* **2009**, 21(early view), doi:10.1002/adma.200803184.

11:00am **IJ+BI+MN+SE+AS-ThM10 Development of an Inkjet Printed Drug Formulation**, ***N. Scoutaris***, *C.J. Roberts, M.R. Alexander,* Nottingham University, UK, *P.R. Gellert*, AstraZeneca, UK

The potential application of ink-jet printing technology as a novel drug formulation technique is examined in this study. Since the inkjet printing technology offers high accuracy of fluids, a success implementation of the project can offer the capability to produce precise amounts of medicines, tailored for each patient.

Felodipine, an antihypertensive drug, was used as an example of an active pharmaceutical ingredient (API), and polyvinyl pirrolidone (PVP) as an excipient. These were dissolved at various ratios in a mixture of ethanol and DMSO (95/5). Using a piezoelectric driven dispenser, picolitre size droplets of the solutions were dispensed onto suitable hydrophobic substrates. The dried products were characterized using AFM, localized nano-thermal analysis and high resolution vibrational spectroscopy (ATR-IR and Raman). Results indicate intimate mixing of the micro-dot API and excipient mixtures. Specifically, ATR-IR confirmed the interaction of felodipine and PVP by means of hydrogen bonding. Nanothermal analysis indicates a single glass transition point which is lowered as the API concentration increases. Finally, confocal Raman microscopy mapping on single droplets allows the visualization of the homogeneous distribution of the drug. These results are a promising first step to ink jet printing of pharmaceuticals.

References

1. Peter A. Melındez, et al., Thermal inkjet application in the preparation of oral dosage forms: Dispensing of prednisolone solutions and polymorphic characterization by solid-state spectroscopic techniques. *Journal of Pharmaceutical Sciences*, 2007. **97**(7): p. 2619 - 2636.

2. Karavas, E., et al., Investigation of the release mechanism of a sparingly water-soluble drug from solid dispersions in hydrophilic carriers based on physical state of drug, particle size distribution and drug-polymer interactions. *European Journal of Pharmaceutics and Biopharmaceutics,* 2007. **66**(3): p. 334-347.

3. Karavas, E., et al., Combining SEM, TEM, and micro-Raman techniques to differentiate between the amorphous molecular level dispersions and nanodispersions of a poorly water-soluble drug within a polymer matrix. *International Journal of Pharmaceutics, 2007.* **340**(1-2): p. 76-83.

11:20am **IJ+BI+MN+SE+AS-ThM11 Fabrication of Plastic Biochips via *in situ* Inkjet Oligonucleotide Array Synthesis***, **I. Saaem**, K. Ma, J. Tian*, Duke University

With the foreseeable integration of microfluidics and microarrays, polymers stand to play a critical role. Generally, arrays are constructed on glass, silicon, membranes, or polyacrylamide matrices. The preference of such materials makes the marriage of arrays and microfluidics fraught with challenges such as developing low-cost manufacturing methods and simultaneously scaling rapidly for diverse applications and chip designs. In addition, deposition or synthesis of the requisite biomolecule reliably in defined surface geometries is a challenging task. We try to alleviate these problems by utilizing the steadily maturing art of inkjet printing on polymer substrates. Polymeric, or plastic, biochips have several advantages in cost, durability, the ability to scale to industrial techniques and possibly serve as disposable point-of-care devices. In our studies, we utilized an inkjet based *in situ* oligonucleotide synthesis platform that uses salvaged printheads from commercial printers. The platform utilizes standard four-step phosphoramidite chemistry with some modifications in order to synthesize oligonucleotides on functionalized substrates. A sensitive pressurization system is used to ensure print quality and an on-board vision system enables substrate registration and synthesis monitoring. Using this platform we synthesized oligonucleotides on prepatterned functionalized plastic slides. Such patterned substrates help in proper droplet formation and fluid mixing on the surface while mitigating satellite and irregular drops, which can lead to cumulative synthesis errors. Functional integrity of synthesized oligonucleotides was confirmed by hybridization with complementary strands. Being able to hot emboss microfluidic structures directly onto plastic slides in combination with the ability to generate arbitrary sequences provides diagnostic capabilities as well as the means to harvest pools of cheap oligonucleotides on demand. Importantly, our results show that the combination of technologies presented is a suitable strategy of fabricating plastic biochips at a cost-effective industrial scale.

11:40am **IJ+BI+MN+SE+AS-ThM12 Study on the Effects of Particle Size and Substrate Surface Properties on the Deposition Dynamics of Inkjet-Printed Colloidal Drops for Printable Photovoltaics Fabrication***, S. Biswas, **Y. Sun***, Binghamton University

Using fluorescence microscopy, the inkjet deposition dynamics of monodispersed polystyrene particles in the size range of 0.02 to 1.1 µm have been studied on glass, Ar plasma cleaned glass, and PDMS coated glass substrates. The results show that the substrate properties play an important role in determining the final dried patterns formed by the colloidal particles. Our observations also reveal that particle size and contact angle formed by the solvent in the dispersion determine how close to the contact line the particles can be deposited. It is found that the diameter of the dried deposited features decrease with the increase in hydrophobicity of the substrates, irrespective of particle sizes. On Ar plasma treated glass ($\theta_A = 13°$), the smaller particles (0.02 & 0.2 µm) show larger depositions than the bigger 1.1 µm particles. Similar type of behavior of the dried deposited features are also observed on clean glass samples ($\theta_A = 36°$). In contrast, on PDMS coated glass ($\theta_A = 111°$), the behavior of the contact line diameter with the evaporation of the drop is similar for all types of particles. On an average, the diameters of the dried deposited features on PDMS coated glass substrates are independent of particle sizes. This study can serve as a realistic experimental model system for a number of fundamental queries on how the final deposition microstructure depends on the ink formulation and substrate properties. The knowledge obtained here can be explored further to optimize process parameters for the fabrication of hybrid solar cells with improved morphology and device properties.

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: C4 - Session IS+SS-ThM

In-Situ Spectroscopy - Interfacial Science & Catalysis
Moderator: D.R. Baer, Pacific Northwest National Laboratory

8:00am **IS+SS-ThM1 Reduction of Cationic Sn in SnO$_x$/PtSn Alloy Surfaces***, G. Liu,* Lehigh University*, H. Bluhm,* Lawrence Berkeley National Laboratory*, **B. Koel***, Lehigh University

Understanding mechanisms of catalyst selectivity requires improved knowledge of oxidation and reduction reactions that occur at the metal/metal oxide interface. We describe studies that probe the thermal stability and reducibility of cationic Sn at SnO$_x$/PtSn alloy interfaces for several different and well-defined surface phases of SnO$_x$ that can be formed depending on the temperature. Our investigations covered a wide range of conditions, from vacuum to the chemical changes during exposures to H$_2$ at pressures up to 5 Torr by using in-situ high pressure photoelectron spectroscopy (HPPES). We find enormous differences in the reducibility of cationic Sn species showing that local surface structure and composition plays an key role in governing these reactions. These studies help to define the overall chemical reactivity of SnO$_x$ species at these interfaces, and in particular, clarify the role of reduced and cationic Sn sites in selective hydrogenation of crotonaldehyde.

8:20am **IS+SS-ThM2 In-situ Study of the Oxidation of Pt(110)***, **M. Grass**, D. Butcher, F. Aksoy, H. Bluhm, G.A. Somorjai, Z. Hussein,* Lawrence Berkeley National Laboratory*, B.S. Mun,* Hanyang University, Korea*, Z. Liu*, Lawrence Berkeley National Laboratory

The formation of oxides on transition metal surfaces has been actively studied because of its importance in understanding heterogeneous catalytic reactions on metal surfaces. In particular, the study of surface oxides on Pt(110) has received much attention. Oxidation reactions over Pt are both industrially significant and fundamentally intriguing. In particular, there has recently been much debate over the surface structure and reaction mechanism of CO oxidation at high O2/CO ratios on Pt(110).

In this study, we used both ambient pressure x-ray photoelectron spectroscopy (AP-XPS) and high pressure scanning tunneling microscopy (HP-STM) to investigate oxidation of Pt(110) as a function of O2 pressure, temperature and gas composition (CO, O2). AP-XPS results demonstrate that two different surface oxygen species form on Pt(110) surface above 500 mTorr O2: chemisorbed oxygen and an island structured species that extends at least two Pt layers deep. HP-STM images under the same conditions confirm the formation of these oxide islands. We present here the pressure and temperature dependence of both oxygen species as well as kinetic measurements of the reaction COad + Oad → CO2 for each of the adsorbed oxygen species.

The Advanced Light Source is supported by the Director, Office of Science, Office of Basic Energy Sciences, of the U.S. Department of Energy under Contract No. DE-AC02-05CH11231.

8:40am **IS+SS-ThM3 Composition and Chemistry of the Liquid/Vapor Interface by In-Situ X-ray Photoelectron Spectroscopy***, **J.C. Hemminger***, University of California, Irvine **INVITED**

We use synchrotron based x-ray photoelectron spectroscopy (XPS) experiments to study the composition and chemistry at the liquid/vapor interface of aqueous solutions. These experiments are motivated by an interest in the fundamental behavior of aqueous interfaces as well as applications to aqueous aerosols in the atmosphere. We take advantage of the variable energy characteristic of synchrotron radiation to carry out XPS experiments as a function of experimental probing depth, thereby generating a depth profile of the liquid/vapor interface. Recent experiments in which we have studied the composition of aqueous salt solutions in the presence of organic surfactants will be described. In addition, studies of acid/base equilibria at the liquid/vapor interface will be described. Our depth profile experiments show that the acid/base equilibrium at the solution surface is modified by the differences in bulk solubility of the acid and base involved in the equilibrium. Two different experimental approaches have been used: an ambient pressure end station at the Advanced light source is equipped with a differentially pumped electron energy analyzer allowing studies with the sample chamber at pressures of a few torr. This system has been used to study saturated aqueous solutions of alkali halide salts. A liquid/jet endstation at the BESSY synchrotron has allowed us to study the surface segregation of molecular ions such as nitrate in aqueous solutions as a function of solution concentrations.

9:20am **IS+SS-ThM5 Oxidation Studies of Gold by in Situ High-Pressure X-ray Photoelectron Spectroscopy***,* ***F. Borondics****, P. Jiang,* Lawrence Berkeley National Laboratory*, S. Porsgaard,* Lawrence Berkeley National Laboratory & iNANO University of Aarhus, Denmark*, M. Köber, A. Caballero, H. Bluhm, M. Salmeron*, Lawrence Berkeley National Laboratory

The high catalytic activity of nanometer size gold particles in various chemical reactions has been intensively investigated in the recent years. However the origin of the exceptional catalytic properties of Au is still strongly debated in many cases ranging from the mobilization of gold under catalytic conditions through the oxidation state of the active Au species during the reaction.

In this study we focus on the interaction of oxygen with Au that has been proposed to play an important role in the mechanism of oxidation reactions. Using in situ high-pressure X-ray photoelectron spectroscopy (HP-XPS) and in situ scanning electron microscopy we studied the different model systems, such as bulk gold, evaporated sub-monolayer and different size nanoparticle samples using single crystalline TiO2 (110) as substrate.

Our results show that gold oxidation can be induced under certain conditions, such as high intensity X-rays or reactive ozone atmosphere. The existence of gold oxide has been mentioned in the literature, but our systematic studies provide a better understanding of the formation and stability of this compound, which is not only a chemical curiosity being the oxide of the noblest metal, but can be very important in designing more efficient catalysts. In addition, we would like to draw the attention of the community to a number of artifacts that can easily lead to misinterpretation of experimental data.

The implications of our results should be considered in the field of catalysis, nano- and surface science as well as in situ high-energy spectroscopies.

9:40am **IS+SS-ThM6 Anchoring of N3 Dye Molecule on TiO_2(110) Surface and its Influence on Energy Level Alignments***,* ***P. Nachimuthu****,* Pacific Northwest National Laboratory*, Z.Q. Yu,* Nanjing Normal University, China*, Z. Zhu, K.M. Beck, S. Thevuthasan, M.A. Henderson*, Pacific Northwest National Laboratory

In dye-sensitized solar cells, the electronic coupling between the dye-sensitizer and TiO_2 determines the alignment of energy levels and the electron transfer dynamics. This electronic coupling is strongly modified by the way in which the dye molecules are adsorbed and anchored to TiO_2 surface, its relative orientations and geometrical structures. The present study is an attempt to understand how the dye molecules are bound to TiO_2 single crystal surface and their influence on the energy level alignments and electron transfer dynamics. Controlled adsorption of dye molecules (bis(4,4'-dicarboxy-2,2'-bipyridine)-bis(isothiocyanato)ruthenium(II) is known as N3) onto TiO_2 surface has been carried out to obtain desired anchoring and orientations by varying the concentration, hydrophobic substituents on dye and defect concentrations (in TiO_2). ToF-SIMS and PEEM mapping techniques were used to understand the distribution of dye molecules on TiO_2 surface. The XPS and UPS measurements were carried out to determine the structural and electronic properties including the stoichiometry of dye molecules on TiO_2 surface, the relative energy levels and band offsets in the absence and presence of UV light. The XPS results show that the atomic ratios of S to Ru and N to S are ~1 and ~5, respectively, which correspond to a non-stoichiometric composition of N3 molecule on TiO_2 surface. The theoretical atomic ratios of S to Ru and N to S in N3 molecules are 2 and 3, respectively. This suggests that an isothiocyanide group from N3 molecule is lost from the surface of TiO_2. The XPS from multilayers of N3 molecules on Si surface however show stoichiometric composition.

10:40am **IS+SS-ThM9 Scanning Transmission X-ray Microscopy of Inorganic and Organic Nanoparticles in the Environment***,* ***S.C.B. Myneni***, Princeton University **INVITED**

Inorganic and organic nanoparticles are common in the environment, and play an important role in the biogeochemical reactions occurring in the natural systems. However, their chemistry and behavior are poorly understood. Using STXM, researchers can examine the chemistry and mineralogy of these particles, and the functional group chemistry of associated organic molecules. While XANES spectral features are used routinely to identify the oxidation states of elements in minerals successfully, fine variations in spectral features of minerals can be used in the identification of minerals and the crystallinity of precipitates/nanoparticles. The XANES spectra are also sensitive to different functional groups and their protonation (or deprotonation) and metal complexation; unique features in XANES spectra can also be used in mapping the distribution and relative concentrations of organic molecules and their complexes at a resolution better than 25 nm in environmental samples. In the last 4-5 years, we made significant progress in the understanding of the mineralogy and chemistry of important environmental nanoparticles and biominerals because of the development of STXM capabilities. A summary of applications of STXM in studying environmental nanoparticles, and highlights of some of these recent findings will be discussed.

11:20am **IS+SS-ThM11 In-situ Characterization of Arsenic on Model Iron Oxide Surfaces**, ***S. Kaya****, F. Mbuga,* SLAC National Accelerator Lab*, T. Kendelewicz,* Stanford University*, J. Newberg, H. Bluhm,* Lawrence Berkeley National Lab*, H. Ogasawara,* SLAC National Accelerator Lab*, G.E. Brown,* Stanford University*, A. Nilsson*, SLAC National Accelerator Lab

Natural contamination of groundwater by arsenic has become an important water quality problem in many parts of the world [1]. Arsenite [As(III)] and arsenate [As(V)] are highly toxic inorganic arsenic species that represent a potential threat to the environment and human health. Iron oxides play a significant role in controlling dissolved As concentration and limit the mobility and availability of As(III) and As(V). Arsenic adsorption mechanisms involve exchange of the As species for surface water and surface OH groups therefore in-situ characterizations of iron oxide surfaces in the presence of water are crucial.

We have studied chemical nature of As on Fe_3O_4(111) and Fe_3O_4(111)/$Fe(OH)_x$ thin films in the presence of water (P<0.5 Torr) using Ambient Pressure Photoemission Spectroscopy (APPES) at Advanced Light Source (ALS) [2]. Hydroxylation of pristine Fe_3O_4(111) surface commences at low relative humidity (RH) values and is followed by adsorption of molecular water with increasing RH. In 0.5 Torr water H_2O:OH ratio at room temperature is about one and all acidic sites are fully hydroxylated. As 3d spectra taken in presence of 0.5 Torr water suggests that oxidation state of arsenic depends on degree of hydroxylation of iron oxide surfaces studied. In addition to the hydroxylation process, increasing RH leads to oxidation of arsenic from As(III) to As (V). Fe^{2+} surface sites plays an important role in the oxidation states of arsenic and the reasons of which will be discussed based on the changes in formal charges during hydration-dehydration processes.

[1] R. Nickson, et. al., Nature, *395* 338 (1998).

[2] H. Bluhm et al., MRS Bulletin, *34* 1022 (2007).

11:40am **IS+SS-ThM12 Kinetic Studies of the Dissociation of Molecular Oxygen on Pt(111)***, H. Ogasawara, L.-Å. Näslund,* ***D.J. Miller****, T. Anniyev, A. Nilsson*, Stanford Synchrotron Radiation Lightsource

Thermally programmed X-ray photoelectron spectroscopy was used to study the dissociation of molecular oxygen on Pt(111) under ultrahigh vacuum conditions. Sub-monolayer coverages of molecular oxygen were dosed onto a clean crystal of Pt(111) at 60 K, a temperature well below the dissociation onset of roughly 95 K. Kinetic analysis of the XPS data indicate that they are consistent with a barrier to O_2 dissociation that is less than 0.4 eV. This result is in striking contrast to the most recent theoretical studies with density functional theory, which all indicate barriers in excess of 0.5 eV (0.5 - 0.9 eV). On the basis of this low observed barrier, we speculate that the direct dissociation of molecular oxygen could be a viable alternative to the associative and peroxide pathways that are presently assumed to be operative in the oxygen reduction reaction.

Magnetic Interfaces and Nanostructures
Room: C1 - Session MI-ThM

Magnetization Dynamics, Imaging and Spectroscopy
Moderator: A.T. Hanbicki, Naval Research Laboratory

8:00am **MI-ThM1 Correlated Magnetic Domain Structure and Magnetic Anisotropy Studies on Epitaxial Au / FePd(001) / MgO(001) Thin Films**, ***J.R. Skuza****, *C. Clavero, K. Yang,* College of William & Mary*, B. Wincheski,* NASA Langley Research Center*, R.A. Lukaszew*, College of William & Mary

The FePd alloy system can exhibit the $L1_0$ chemically ordered phase when the Fe:Pd stoichiometry of the alloy is near 1:1.[1] The crystallographic structure of the $L1_0$ ordered alloy is characterized by alternating Fe and Pd atomic layers along a cubic stacking direction, which as a consequence suffers a tetragonal distortion. This tetragonal distortion induces a strong perpendicular magnetic anisotropy (PMA) when the layering is parallel to the film plane and the material is in thin film form. The origin of the strong PMA is the large spin-orbit coupling of the paramagnetic Pd atoms and a strong hybridization of their *4d* bands with the highly polarized Fe *3d* bands.[2] Although the mechanism of PMA is well known, controlling it in thin film form is non-trivial and warrants further study to be useful in applications such as magneto-recording media.

We will report on our correlated studies of the magnetic domain structure with the PMA in epitaxial Au / FePd(001) / MgO(001) thin films. Epitaxial FePd thin films were grown using magnetron sputtering in an ultra-high vacuum deposition system at elevated temperatures (400 – 600 °C) and on MgO(001) substrates to achieve highly ordered films with strong PMA. The films were subsequently capped with Au at room temperature (RT) to prevent oxidation, and alteration of the magnetic anisotropy.[3] Reflection high energy electron diffraction was used *in situ* to monitor the epitaxial growth and x-ray diffraction techniques were used *ex situ* to monitor the chemical ordering of the films. Magnetic anisotropy values were obtained from hysteresis loops measured at RT using a Superconducting Quantum Interference Device magnetometer and also by ferromagnetic resonance scans. The magnetic domain structure was investigated using a Nanotec scanning probe microscope with a magnetically coated tip in non-contact mode. These studies have improved our understanding of these strong PMA materials, enabling correlations between the observed domain structure and the magnetic anisotropy, along with comparison to models of domain structure.[4]

[1] T. B. Massalski *et al.* (eds.), Binary Alloy Phase Diagrams, (ASM International, 1990), p. 1751.

[2] A. Cebollada *et al.*, Magnetic Nanostructures, edited by H. S. Nalwa (American Scientific Publishers, 2002), pp. 94-100.

[3] C. Clavero *et al.*, Appl. Phys. Lett. **92**, 162502 (2008).

[4] A. Hubert and R. Schafer, Magnetic Domains The Analysis of Magnetic Microstructures (Springer, 2000), pp. 107-354.

This work was supported by the Virginia Space Grant Consortium, National Science Foundation (DMR Grant #0355171), the American Chemical Society (PRF Grant #41319-AC), and the Research Corporation Cottrell Scholar Award.

8:20am **MI-ThM2 Dependence of the Domain Wall Pinning Strengths to Lateral Constriction Size and Electrical Bias in GaMnAs**, ***S.U. Cho***, *H.K. Choi, Yang, Park,* Seoul National University, Korea*, F. DaSilva, T. Osminer, D.P. Pappas*, National Institute of Standards and Technology

Dynamics of domain wall (DW) motion and spin-polarized transport across DWs have received much attention due to their potential applications in large-scale memory storage and logic devices. Particularly for GaMnAs, spin-polarized current induced magnetization switching has been demonstrated [1]. Lateral nanoconstrictions (NC), from which DWs can form and be pinned, in GaMnAs have been utilized to demonstrate nonvolatile memory elements [2] as well as structures showing large magneto-resistances (MRs) [3]. Here, we investigate the size dependence of constrictions in GaMnAs epifilms, particularly the dependence of DW pinning strength as function of lateral constriction size, as well as electrical bias across the constriction. A method to realize nanoconstrictions without plasma-assisted methods and nonlinear IV transport across NC junctions have been reported previously [4]. For this study, we present magnetotransport measurements on identically sized constrictions in series (up to five NC in series) equally spaced apart (~ 2 microns). For large constrictions, the overall resistance (<25 kΩ at room temperature) as function of applied field shows a background negative MR response which can be attributed to anisotropic magnetoresistance with distinct jump-down behavior. The number of distinct jump-down behavior corresponds to number of NC plus one with little dependence of jump field to bias current. Thus, for large constrictions, the geometrical lateral constrictions act 'to seed' DWs. For smaller constrictions (overall resistance > 25 kΩ at room temperature), the MR response is more complex as DW are formed and pinned at the lateral constrictions. MR responses show jump-up behavior along with a complex dependence on jump field to bias current. Furthermore, we will discuss the complex switching behavior observed in small constrictions in series in terms of effects attributed to DW motion and spin-polarized transport across DWs.

[1] M. Yamanouchi *et al.*, Nature **428**, 539 (2004).

[2] K. Rappert *et al.*, Nat. Phys. **3**, 573 (2007).

[3] C. Rüster *et al.*, Phys. Rev. Lett. **91**, 216602 (2003); A.D. Giddings *et al.*, Phys. Rev. Lett. **94**, 127202 (2005).

[4] S.U. Cho *et al.* Appl. Phys. Lett. **91**, 122514 (2007).

8:40am **MI-ThM3 Racetrack Memory: A Current Controlled Domain Wall Shift Register**, ***S.S.P. Parkin***, IBM Almaden Research Center **INVITED**

Racetrack Memory[1] promises a novel storage-class memory with the low cost per bit of magnetic disk drives but the high performance and reliability of conventional solid state memories. Unlike conventional memories, the fundamental concept of Racetrack Memory is to store multiple data bits, perhaps as many as 10 to 100, per access point, rather than the typical single bit per transistor. In Racetrack Memory the data is stored in the form of a series of magnetic domain walls along magnetic nanowires which are oriented either parallel or perpendicular to the surface of a silicon wafer. These distinct structures form "horizontal" and "vertical" Racetrack Memories. Conventional CMOS devices and circuits are used to provide for the creation and manipulation of the domain walls in the magnetic nanowires or "racetracks". The domain walls are shifted back and forth along the nanowires using nano-second long current pulses via the transfer of spin angular momentum from the spin polarized current. Note that the shifting of neighboring domain walls in the same direction along a nanowire is not possible using conventional means of manipulating domain walls with localized magnetic fields.

In this talk we discuss progress towards building a Racetrack Memory and the fundamental physics underlying it. In particular, we discuss the current and field controlled dynamical motion of magnetic domain walls in magnetic nanowires formed from permalloy and related materials.

[1] S.S.P. Parkin, M. Hayashi and L. Thomas, Science **320**, 190 (2008); S.S.P. Parkin, Scientific American (June, 2009).

9:20am **MI-ThM5 Localized Magnetic and Electric Field Response in Mesoscopic InAs Quantum Well Hall Crosses**, ***M. Nishioka****, L. Folks, J. Katine, E.E. Marinero, B.A. Gurney*, Hitachi GST

Transport properties of mesoscopic Hall crosses in localized magnetic and electric fields have received considerable attention because of their potential application to detection of localized magnetic fields with nanometer resolution. We recently made the first measurement of the response of the Hall voltage to the localized magnetic and electric fields in Hall crosses down to 50 nm x 50 nm cross-sections [1]. Hall crosses, based on InAs quantum well heterostructures, were scanned with a magnetically-coated probe which was also electrically gated to generate both localized electric and magnetic fields. We found that the Hall crosses were sensitive to magnetic fields at the center of the cross. Also, the sensitivity to the localized magnetic field was found to be much larger than that to the localized electric field.

In this work, we report the response to localized magnetic and electric fields of similar crosses configured electrically in "the bend resistance (BR) geometry", where current is passed between adjacent arms of the cross and a voltage is measured between the remaining arms. To our knowledge the response of such heterostructures in the BR configuration to localized magnetic and electric fields has not been previously reported. Figure 1 shows the BR response when the gate voltage applied to the probe and the current applied to the Hall cross are 1 V and -600 μA, respectively. The magnetic field created by the magnetic tip at the InAs quantum well is ~ 600 Oe. The prominent feature in this image is that the BR is sensitive to the localized fields both at the center and the two corners. This is quite different from the response of the Hall resistance [1] where magnetic sensitivity was predominant at the cross center. By using both non-magnetic and magnetic probes, we have found that the response to localized electric fields is comparable to localized magnetic fields. Thus, the mapping in Fig. 1 shows significant contributions from both fields. It may therefore be possible to combine the electric field sensitivity of BR measurements with

---

* Falicov Student Award Finalist

conventional Hall measurements to obtain localized electric and magnetic field information on the nanometer size scale from the same device.

[1] L. Folks *et. al.*, “Near-surface nanoscale InAs Hall cross sensitivity to localized magnetic and electric fields”, accepted by Journal of Physics: Condensed Matter.

9:40am **MI-ThM6 Isolation of Exchange- and Spin-orbit- Driven Effects via Manipulation of the Axis of Quantization**, *T. Komesu,* ***G.D. Waddill***, Missouri University of Science and Technology, *S.W. Yu, M.T. Butterfield, J.G. Tobin*, Lawrence Livermore National Laboratory

Double Polarization Photoelectron Spectroscopy (DPPS), using circularly polarized xrays and true spin detection, has been performed using the 2p core levels of ultra-thin films of Fe and Co. This includes both the separation into magnetization- and spin- specific spectra and an Instrumental Asymmetry analysis. By simply by choosing different axes of quantization it is possible to selectively manipulate the manifestation of exchange and spin-orbit effects. Furthermore, the underlying simplicity of the results can be confirmed by comparison to a simple yet powerful single-electron picture.

The interplay of spin-orbit and exchange effects is of crucial importance to the understanding of complex electronic structure. For example, in the highly relativistic 5f systems, this interplay may be the key to understanding electron correlation. [1] One way to address this crucial issue is via photon-helicity- specific and spin-polarized photoemission from core levels, which is strongly dependent upon each of the two effects. [2] In fact, it is possible to observe strongly spin polarized photoemission from completely “non-magnetic” systems. [3] Here, using circularly polarized x-rays and true spin detection, it will be demonstrated how each of the effects, exchange and spin-orbit, can be isolated and quantified, simply by choosing different axes of quantization within the same overall experimental geometry. Moreover, the underlying simplicity of the results will be illustrated by the utilization of separate magnetization- and spin-specific spectra, as well as a simple but powerful single-electron model.

Takashi Komesu: Present address: Spring8, Japan Synchrotron Radiation Research Institute, Japan

Corresponding Author, Tobin1@LLNL.Gov

Lawrence Livermore National Laboratory is operated by Lawrence Livermore National Security, LLC, for the U.S. Department of Energy, National Nuclear Security Administration under Contract DE-AC52-07NA27344. This work was supported by the DOE Office of Basic Energy Science and Campaign 2/WCI/LLNL. The APS has been built and operated under funding from the Office of Basic Energy Science at DOE. We would like to thank the scientific and technical staff of Sector 4 of the Advanced Photon Source for their technical assistance in supporting this work. TK would like to thank Prof. Peter A. Dowben at University of Nebraska-Lincoln for valuable scientific discussions.

References

1. S.-W. Yu et al, J. Phys. Cond. Mat. 20, 422202 (2008) and ref’s therein.
2. J.G. Tobin and F.O. Schumann, Surface Science 478, 211 (2001).
3. S.W. Yu et al, Phys. Rev. B 73, 075116 (2006); J.G. Tobin et al, EuroPhysics Lett. 77, 17004 (2007).

10:40am **MI-ThM9 Magnetic Soft X-ray Microscopy: Challenges and Opportunities to Image Fast Spin Dynamics on the Nanoscale**, ***P.J. Fischer***, Lawrence Berkeley National Laboratory **INVITED**

The manipulation of spins on the nanoscale is of both fundamental and technological interest. In spin based electronics the observation that spin currents can exert a torque onto local spin configurations which can e.g. push a domain wall has stimulated significant research activities to provide a fundamental understanding of the physical processes involved.

Magnetic soft X-ray microscopy is a powerful analytical technique since it combines X-ray magnetic circular dichroism (X-MCD) as element specific magnetic contrast mechanism with high spatial and temporal resolution. Fresnel zone plates used as X-ray optical elements provide a spatial resolution down to currently <15nm [1] thus approaching fundamental magnetic length scales such as the grain size [2] and magnetic exchange lengths. Images can be recorded in external magnetic fields giving access to study magnetization reversal phenomena on the nanoscale and its stochastic character [3] with elemental sensitivity [4]. Utilizing the inherent time structure of current synchrotron sources fast magnetization dynamics with 70ps time resolution, limited by the lengths of the electron bunches, can be performed with a stroboscopic pump-probe scheme.

I will review recent achievements with focus on current induced wall [5] and vortex dynamics in ferromagnetic elements [6].

Future magnetic microscopies are faced with the challenge to provide both spatial resolution in the nanometer regime, a time resolution on a ps to fs scale and elemental specificity to be able to study novel multicomponent and multifunctional magnetic nanostructures and their ultrafast spin dynamics. The unique features of soft X-ray microscopy and the current developments with regard to improved X-ray optics and high brilliant fsec X-ray sources seems to make this technique a strong candidate to meet this challenge.

Collaboration with M.-Y. Im, B.L. Mesler, W.Chao (CXRO), G. Meier, L. Bocklage, M. Bolte, R.Eiselt, B. Krueger, D. Pfannkuche, U. Merkt (U Hamburg), S. Kasai, K. Yamada, K. Kobayashi, T. Ono (U Kyoto), Y. Nakatani (U Chofu), H. Kohno (U Osaka), A. Thiaville (U Paris-Sud), D.H. Kim (Chungbuk U) and S.-C. Shin (KAIST) is greatly appreciated. Supported by the Director, Office of Science, Office of Basic Energy Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy.

References

[1] D.-H. Kim, et al., J. Appl. Phys. **99**, 08H303, (2006)

[2] M.-Y. Im, et al, Advanced Materials **20** 1750 (2008)

[3] G. Meier et al., Phys. Rev. Lett. **98**, 187202 (2007)

[4] M.-Y. Im, et al., Phys Rev Lett **102** 147204 (2009)

[5] L. Bocklage, et al., Phys Rev B **78** 180405(R) (2008)

[6] S. Kasai, et al., Phys Rev Lett **101**, 237203 (2008)

MEMS and NEMS
Room: A8 - Session MN+GR-ThM

Graphene and Carbon Based MEMS/NEMS Devices
Moderator: B.R. Ilic, Cornell University

8:00am **MN+GR-ThM1 Graphene Mechanics, Tribology, and NEMS Resonators**, ***J. Hone***, Columbia University **INVITED**

This talk will describe our work toward fundamental understanding of the mechanical and and tribological properties of graphene, and its application in nano-electromechanical devices (NEMS). We have used nanoindentation to measure the elastic stiffness and ultimate strength of single graphene sheets^1. These measurements show that graphene is the strongest material ever measured, with an ultimate strength of 130 GPa at an ultimate strain of over 25%. As such, it is the first material whose mechanical properties can be probed deep into the nonlinear elastic regime. We have also measured the frictional behavior of graphene and other related two-dimensional materials. These materials all show an unexpected strong dependence of the frictional force the number of atomic layers, with thinner samples demonstrating larger friction. Finally, we have demonstrated electronic readout of graphene nanomechanical resonators. These devices show highly tunable mechanical resonances in the range 20-300 MHz, with large output signal compared to other NEMS of comparable size. The quality factor of these resonators increases from ~100 at room temperature to ~10,000 at low temperature. The measured sensitivity of these resonators to applied mass shows their promise as multifunctional sensors.

[1] Changgu Lee, Xiaoding Wei, Jeffrey Kysar, J. Hone, “Measured elastic properties and ultimate strength of monolayer graphene,” *Science* **321**, 385 (2008)

8:40am **MN+GR-ThM3 Enhanced Stabilities in Resonant Response of Carbon Nanotube Network Reinforced Al Thin-Film Nanomechanical Resonators**, ***Y.D. Kim***, *J.H. Bak, J. Lee, S.R. Lee, K. Char, S. Hong, Y.D. Park*, Seoul National University, South Korea

With superior mechanical properties, single-walled carbon nanotubes (swCNT) are an attractive reinforcement component for nanoscale composites, based in either polymer or metal matrices [1]. Recently enhancements in mechanical properties of metallic thin-films reinforced by CNTs have been reported [2]. Self-consistent results from quasi-static and dynamic flexural measurements indicate the elastic modulus to nearly double with the inclusion of self-assembled swCNT network layer in Al thin-films [3]. Here, we present significant enhancements in resonant frequency stability of CNT network reinforced Al thin-film nanomechanical resonators. We characterize the stability in the resonant response either by long-cycle measurements or with applied stress. Long-cycle (>10^{11}) dynamic flexural measurements show suppression of anelastic effects, which limits the applicability of metallic thin-films nanomechanical resonators. Application of stress is accomplished by two differing methods. A tensile stress is applied by using a ‘chip-bending’ method. A compressive stress is applied through thermal-elastic effects from Joule heating. For both cases, a significant stability in CNT network reinforced Al thin-film resonant response is observed.

[1] W.A. Curtin and B.W. Sheldon, Materials Today 7, 44 (2004); J.N. Coleman et al., Advanced Materials 18, 689 (2006).

[2] Kang et al., Advanced Materials 19, 427 (2007).

[3] J.H. Bak, Y.D. Kim, et al., Nature Materials 7, 459 (2008).

9:00am **MN+GR-ThM4 Carbon Nanostructures on Microscrolls**, ***J.W. Choi***, Kyung Hee University, Republic of Korea

Thin bimetallic films on silicon substrates are formed in microscale scroll when the substrate temperature varies. To increase the functional properties of the bimetallic scroll, carbon nanostructures are directly integrated to the scroll. The formation of the bimetallic scroll and the direct integration of carbon nanostructures are studied for various apllications including NEMS, sensors, energy storage devices.

9:20am **MN+GR-ThM5 Thin Smooth Carbon Nanotube/Polymer Composite Membranes**, ***L. Pei***, *R. Vanfleet, M.R. Linford, R.C. Davis*, Brigham Young University

We have developed a new and straightforward method for fabricating freely suspended ultrathin carbon nanotube (CNT) membranes. A smooth transferrable CNT sheet was first made from vertically aligned carbon nanotube (VACNT) forests by placing mixed cellulose ester (MCE) filter paper on a VACNT forest and using a roller to both compress the forest and transfer the nanotubes to the filter paper. The compressed CNT film was then transferred to a solid substrate and the MCE was subsequently dissolved, leaving the CNT film on the substrate. Nanotube – polymer composite films were then fabricated by spin casting a polymer layer on top of the transferred CNT sheet. If the solid substrate was coated with a polymer film prior to CNT transfer, a polymer/CNT/polymer sandwich was created. The composite membranes were subsequently released from the substrate. Characterization of the films and membranes preformed by scanning electron microscopy, atomic force microscopy, and by strength testing will be presented.

9:40am **MN+GR-ThM6 Nanostructuring of Ultrananocrystalline Diamond (UNCD) Thin Films Via Block Copolymer Lithography**, ***M. Ramanathan***, *S.B. Darling, A.V. Sumant, O.H. Auciello*, Argonne National Laboratory

Diamond is in many ways an optimal material for numerous technological, industrial and biological applications because of its exceptional physical and chemical properties. In addition to high hardness, diamond is stiff, biocompatible and wear resistant. Nanopatterning of diamond surfaces is critical for the development of diamond-based MEMS/NEMS, such as resonators or switches. Micro/nano structuring of diamond materials is typically associated with conventional lithographies such as photolithography or electron beam lithography. In this paper, we demonstrate a simple process, known as block copolymer (BCP) lithography, of nanostructuring ultrananocrystalline diamond (UNCD) surfaces. In BCP lithography, nanoscale self-assembled polymeric domains serve as an etch mask for pattern transfer. We used thin films of a cylinder-forming organic–inorganic BCP, poly (styrene-*block*-ferrocenyldimethylsilane), PS-*b*-PFS, as an etch mask on UNCD. Orientational control of the etch masking cylindrical PFS blocks are achieved by manipulating the polymer film thickness in concert with the annealing treatment. For films much thinner than the equilibrium periodicity of the microdomains, the cylinders spontaneously orient themselves perpendicular to the substrate. On the other hand, films with thickness close to the equilibrium periodicity exhibit in-plane orientation. We have observed that surface roughness of UNCD plays an important role in transferring the pattern. Reactive ion etching (RIE) using oxygen gas was used to etch the exposed areas of UNCD. Arrays of both UNCD posts and wires have been created using the same starting polymeric materials as the etch mask.

10:40am **MN+GR-ThM9 Fabrication of a Reusable Template Based on Ultrananocrystalline Diamond for Electrodeposition of Metal and Semiconductor Micro/Nanowires**, ***D.B. Seley***, *D.A. Dissing,* University of Wisconsin - Stevens Point, *A.V. Sumant, R. Divan, S. Miller,* Argonne National Laboratory, *E.A. Terrell,* University of Wisconsin - Stevens Point, *O.H. Auciello,* Argonne National Laboratory, *M.P. Zach*, University of Wisconsin - Stevens Point

Electrodeposition is a versatile technique that has been used for the synthesis of nanowires. There are several methods available for the synthesis of nanowires, each requiring some form of template, which is not easily reusable. A recent report uses a combination of optical lithography, and the conductive edges of a metal for the deposition of nanowires, but the patterned metal is sacrificial, requiring a multi-step process to regenerate the electrode (1). We demonstrate a top-down approach involving lithography and reactive ion-etching of ultrathin (150 nm) undoped and N-doped ultrananocrystalline diamond (UNCD) stack defining nanoelectrodes for subsequent electrodeposition of micro/nanowires of desired materials. Once this template consisting of arrays of nanoelectrodes of various shapes has been made, it is a permanent reusable template for synthesis of micro- and nanowires. Subsequent manufacture of nanowires becomes almost as simple as using a rubber stamp and ink. The multilayer diamond electrode provides low adhesion to the deposited materials which allows for easy transfer of the resulting electrodeposited micro- or nanostructures onto an adhesive polymer. Each set of structures is removed, regenerating a pristine electrode surface for multiple depositions without needing to repeat the difficult lithography steps for each batch of wires made. The combination of unique electrical and chemical properties of UNCD is promising to allow mass production of uniform patterned nanostructures. Materials electrodeposited until now include: Pb, Au, Cu, Pd, Pt, Co (non-aqueous), Te, CdTe, and CdS.

Acknowledgments

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 No. DE-AC02-06CH11357

Additional support was provided by UPDC Fund (UWSP), WiTAG and University of Wisconsin-System.

1. E. J. Menke, M. A. Thompson, C. Xiang, L. C. Yang and R. M. Penner, *Nature Materials*, **5**, 914 (2006).

11:00am **MN+GR-ThM10 Fabrication and Characterization of Ultrananocrystalline Diamond Nanowires for Developing Next Generation of Nanoelectronic Devices**, ***A.V. Sumant***, *L.E. Ocola,* Argonne National Laboratory, *X.P. Wang,* University of Puerto Rico, *D.O. Lopez, O.H. Auciello, D.C. Mancini*, Argonne National Laboratory

Recently, there is tremendous amount of interest in making diamond nanowires (DNWs) and diamond nano-rods (DNRs), due to their extraordinary mechanical, electrical, and optical properties as predicated by theory, however, synthesizing or fabricating these quasi1-dimensional sp^3 nanostructures is proved to be very challenging. To date, only few attempts have been reported either by etching single crystal diamond from top-down process to produce diamond nano-rods (DNRs) or by coating Si nanowires with nanocrystalline diamond. We report a method based on e-beam lithography and reactive ion etching of ultrananocrystalline diamond (UNCD), to produce UNCD nanowires (UNCDNWs) and UNCD nano-rods (UNCDNRs) with nanowire diameter as small as 20 nm. Since they are produced by lithographic approach, they can be fabricated almost at will in well defined position with nanometer scale precision. We have fabricated Nitrogen doped UNCDNWs and characterized them using Raman spectroscopy (UV and visible) and TEM microscopy. We will discuss about preliminary nanostructural studies of UNCDNWs and electrical measurements. The ability to fabricate UNCDNWs and UNCDNRs gives an opportunity to study fundamental mechanism of transport processes in diamond nanowires, which will enable new ideas and possibility of fabricating new functional nanoelectronic devices and sensors with increased sensitivity for a variety of applications in nanotechnology.

Manufacturing Science and Technology
Room: C3 - Session MS+GR+MI-ThM

Manufacturing Issues for Beyond CMOS Nanoelectronics
Moderator: R.E. Geer, University at Albany

8:40am **MS+GR+MI-ThM3 Spin-Polarized Electrons in Silicon**, ***B. Huang***, *I. Appelbaum*, University of Maryland **INVITED**

In this talk, I will show how ballistic hot electron transport can be used for spin injection and detection in silicon. With this technique, we measure long conduction electron spin lifetimes which enable spin transport in silicon over long distances (up to 2mm). I will also discuss our investigations of spin dephasing and spin precession in oblique magnetic fields, and show how we realized spin precession control with an electric field.

9:20am **MS+GR+MI-ThM5 Methods for Characterizing Variations in Excitation Mode Frequency and Linewidth in Spin Transfer Nanocontact Oscillators**, ***M.R. Pufall***, *W.H. Rippard*, National Institute of Standards and Technology **INVITED**

Resonance probing of magnetoelectronic nanostructures with AC spin torque promises to provide a new means to understand their magnetic behavior, and their interaction with spin-polarized currents. An AC current produces an AC spin polarized current, which in turn produces a time-varying torque. By varying the frequency of the current, the resonance spectrum of the structure can be investigated. By this method, the ferromagnetic resonance mode of metallic and tunnel junction nanopillars has been investigated, and in nanocontact structures, enables probing the ferromagnetic resonance and damping of continuous films at unprecedented length scales.

However, for this tool become the more generally useful, the details of the signals produced by AC spin torque must be better understood. Beyond the ferromagnetic resonance mode, other responses are observed that have not been predicted; in nanocontacts, due to the unbounded geometry, prediction of modes beyond the ferromagnetic resonance in even more difficult. Furthermore, the shape of the ferromagnetic resonance line itself can vary in a complicated way, depending on the sample geometry and materials. As a step towards the goal of developing a robust tool that gives quantitative information about nanocontact spin transfer oscillators, I will present AC spin torque measurements from a variety of field geometries, and of materials with either in- or out-of-plane anisotropy, describing the basic behavior observed in each case. Then, I will compare different methods of ferromagnetic resonance detection (frequency-swept linewidth, field swept linewidth, field or microwave modulation) and discuss the challenges associated with interpreting these results to obtain the damping constant and the zero-field field-swept linewidth.

10:40am **MS+GR+MI-ThM9 Large Area, Continuous Single- and Few- Layer Graphene Films on Insulating Substrates**, ***J. Kong***, Massachusetts Institute of Technology **INVITED**

Graphene has exceptional electronic, thermal and mechanical properties. For the realization of graphene-related applications, it is necessary to develop reliable and low cost fabrication methods of graphene-based structures, ideally on any substrates. In this talk I will present our method of fabricating large area (~cm^2) films of single- to few-layer graphene and transferring the films to arbitrary substrates. The graphene films are synthesized by ambient pressure Chemical Vapor Deposition, consist of regions of 1 to ~10 graphene layers and have an average thickness of 2-3 nm. The structure of the graphene films are characterized with various methods, such as atomic force microscope, transmission electron microscope, scanning tunneling microscope and Raman. Detailed understanding in the growth mechanism provides guidance for improving the quality of the graphene films. The method presented in this work can potentially be scaled to industrial production of graphene films, for applications such as ultra-thin conductive and transparent electrodes, or devices and interconnect for integrated circuits.

11:20am **MS+GR+MI-ThM11 Graphene Nanoelectronics for Post-CMOS Logic Switches**, ***C.Y. Sung***, IBM T.J. Watson Research Center **INVITED**

Electron charge has been the computational state variable for decades. However, a new switch is urgently needed because scaling may fail to keep providing performance-cost benefits. We report the scaling limits and graphene research in monolayer synthesis, transistor engineering and new state variable logic switches. We demonstrate graphene nanoelectronics feasibility by monolayer-control wafer-scale synthesis, high performance device fabrication, bandgap engineering, for low-power, low noise performance and process integration. Computation with less power requires switches with alternative state variables. Graphene, with many desirable properties, emerge as a promising post-CMOS logic candidate.

Nanometer-scale Science and Technology
Room: L - Session NS-ThM

Characterization and Imaging at the Nanoscale
Moderator: C. Nakakura, Sandia National Laboratories

8:00am **NS-ThM1 Depth Resolved Luminescence from ZnO Nanowires**, ***R.A. Rosenberg***, *S. Vijayalakshmi, M. Abu Haija,* Argonne National Laboratory, *J. Zhou, J. Liu, S. Xu, Z.L. Wang*, Georgia Institute of Technology

Nanodevices based on wide bandgap semiconductors have great potential in applications running from photon detectors to gas sensors. Critical to their successful implementation is knowledge of the surface and interfacial properties. In the present work we have utilized the limited penetration depth of soft x-rays (550-1000 eV) to study the near surface properties of vertically aligned ZnO nanowires. For a grazing angle of 5 degrees the penetration depth of these x-rays varies between 11 and 65 nm. Thus by obtaining optical luminescence spectra as a function of energy it is possible to probe the near surface region with nm-scale resolution. We will present energy dependent optical luminescence data from ZnO nanowire samples with diameters of 350 nm, 390 nm and 720 nm. In each case the ratio of the oxygen vacancy luminescence to the near band edge luminescence intensity peaks at an energy corresponding to ~17 nm x-ray penetration. This shows that the nanowires of three different diameters have a near surface defect region with a width of ~20 nm, which agrees with the conclusions from previous photoluminescence and cathodoluminescence studies [1-3]. Applications of this technique to other systems will also be discussed.

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.

REFERENCES

[1] N. Pan et al., J. Phys. Chem. C 111, 17265 (2007).

[2] I. Shalish, H. Temkin, and V. Narayanamurti, Phys. Rev. B 69, 245401 (2004).

[3] J. D. Ye et al., App. Phys. Lett. 92, 131914 (2008).

8:20am **NS-ThM2 Scanning Chemical Microscopy of Nanoscale Roughness Formation in Photoresist Materials**, ***R. Ramos***, *I. Riisness, M. Gordon*, University of California Santa Barbara

Developing a molecular-level understanding of surface chemistry is of critical importance for advancements in the fields of surface science, materials research and catalysis. In particular, the ability to characterize, interrogate and image the chemical composition of surfaces at high spatial resolution would provide greater insight into surface reaction mechanisms and dynamics. For this purpose, optical spectroscopy, when combined with scanning probe microscopy, is a powerful tool for simultaneous chemical identification and imaging of surfaces at the nanoscale. Over the past few years, enhancement of optical fields through plasmonic coupling of light with metal nanostructures has been used for near-field vibrational spectroscopy (e.g., surface- and tip-enhanced Raman spectroscopy – SERS/TERS). However, these techniques have not seen widespread use for surface nanocharacterization because of poor quality field enhancers (i.e., reproducible tips) and difficulties in interpreting spectroscopic data.

In this work, we will show how careful design of the plasmonic properties of the tip and scanning configuration can turn TERS into a robust chemical analysis technique. Our experimental setup combines a tuning fork/cantilever-based scanning probe microscope with in-situ Raman and reflectance spectroscopy; the system also allows simultaneous mechanical and electrical surface interrogation at the nanoscale. In this talk, we will demonstrate that spatially correlating topography with chemical fingerprinting can provide insight into mechanisms of photoresist roughening. This issue is critical in the microelectronics industry as the size of device structures is reduced; specifically, roughness generated during the lithography and plasma etching steps in device fabrication is ultimately transferred into the active parts of the device, leading to lower performance. By combining near-field optical and chemical interrogation with traditional far-field vibrational spectroscopy and X-ray photoelectron spectroscopy, we will highlight the chemical processes involved in roughness formation in advanced photoresist polymers and investigate how they are affected by plasma exposure.

8:40am **NS-ThM3 In Situ Nanoscale Characterization of Gas Fluxes of Organic Membranes by Flux-Lateral Force Microscopy**, ***L.S. Kocherlakota***, *D.B. Knorr, R.M. Overney*, University of Washington

Characterization studies of polymeric membranes for enhancing the gas transport rates are highly significant in current separation technologies.

However transport property analyses like gas permeability measurements are bulk scale methods with limited access to local transport properties in multiphase systems such as nanocomposites membranes. In this context our group has developed a flux-lateral force microscopy (F-LFM) technique[1] for the in situ nanoscale characterization of the membranes, by monitoring the gas fluxes through them on a nanoscale. This technique, which is based on atomic force microscopy (AFM) utilizes the lubricating effect and the mechanical property changes in the membrane to determine fluxes. It was demonstrated by this technique that lateral force *vs.* pressure curves offered a direct measure of local gas permeabilities. In this paper we present the nanoflux analysis in Poly(trimethyl silyl propyne) (PTMSP), a glassy polymer with highest gas permeability of all known synthetic polymeric systems as well as high organic vapor/permanent-gas selectivity. The local fluxes in PTMSP films measured by F-LFM are compared to global fluxes obtained from conventional integrated methods. The sensitivity of F-LFM technique is demonstrated by presenting the reverse selective transport rates of He and CO_2 in PTMSP membranes as detected by the technique. The paper will also address the impact of aging, and flux dependence on film thickness.

Reference:

[1] J.H. Wei, M. He, and R.M. Overney**,** *Direct measurement of Nanofluxes and Structural Relaxations of Perflourinated Ionomer Membranes by Scanning Probe Microscopy,* J.Membrane Sci. **279,** 608-14 (2006)

9:00am NS-ThM4 Nanoscale Electrodes by Conducting Atomic Force Microscopy at Elevated Temperatures

M. Louie, California Institute of Technology*, A. Hightower,* Occidental College*, S. Haile*, California Institute of Technology

The combination of conducting atomic force microscopy (AFM) and electrical measurements (AC impedance spectroscopy and cyclic voltammetry) offers many advantages for measuring fuel cell electrode kinetics. The use of a conducting AFM probe as a nanoelectrode enables isolation and characterization of a single electrode-electrolyte interface without the need for a reference electrode. Furthermore, this technique permits studies of the spatial dependence of mechanistic phenomena while providing controllable electrode-electrolyte contact areas. The feasibility of using a nanoscale probe as a fuel cell electrode has been examined for the polymer electrolyte membrane system at room temperature (1-2). Higher temperature capabilities would make this technique useful for a wide variety of material systems, including low-to-intermediate temperature solid electrolytes.

Here, we demonstrate the viability of conducting AFM under controlled environments and at temperatures relevant to proton conducting solid acid compounds. Solid acid compounds have been demonstrated as viable proton conducting electrolytes for fuel cells (3-4), with peak power densities of ~ 400 mW/cm^2 at ~ 240 ºC (5). Such fuel cells provide several advantages over polymer membrane fuel cells, including improved kinetics due to higher operating temperatures, impermeability of the membrane to fuels, and elimination of the need for complex water management systems. However, activation overpotential losses, particularly at the cathode, limit the performance (6), and electrode kinetics are not yet well understood.

We select cesium hydrogen sulfate, $CsHSO_4$, as a representative solid acid electrolyte for the study of oxygen electroreduction. Experiments are performed with a platinum-coated probe in contact with $CsHSO_4$. The Pt-based counter electrode, which covers the entire opposing area of the electrolyte, is effectively reversible and contributes negligible overpotential to the measurements. We discuss the experimental challenges associated with high impedance systems and mitigation strategies to extract meaningful information. We also present impedance spectra and cyclic voltammograms for Pt|$CsHSO_4$.

1. R. O'Hayre, M. Lee, F. B. Prinz, *J Appl Phys* **95**(12), 8382-8392 (2004)

2. D. A. Bussian, J. R. O'Dea, H. Metiu, S. K. Buratto, *Nano Lett* **7**(2), 227-232 (2007)

3. D. A. Boysen, T. Uda, C. R. I. Chisholm, S. M. Haile, *Science* **303**, 68-70 (2004)

4. S. M. Haile, D. A. Boysen, C. R. I. Chisholm, R. B. Merle, *Nature* **410**, 910-913 (2001)

5. T. Uda and S. M. Haile, *Electrochem Solid State Lett* **8**(5), A245-A246 (2005)

6. S. M. Haile, C. R. I. Chisholm, K. Sasaki, D. A. Boysen, T. Uda, *Faraday Discussions* **134**, 17-39 (2007)

9:20am NS-ThM5 Unraveling Atomic Structures on $CeO_2(111)$ by Dynamic Force Microscopy

M. Reichling, Universität Osnabrück, Germany **INVITED**

Cerium dioxide (ceria) is a material that is widely used for catalytic applications. It is, for instance, an essential part of the 3-way catalytic converter known from automotive technology and holds substantial promise in other diverse research areas like solid-fuel cell technology for the production of hydrogen. In this context, ceria acts as an oxygen buffer as well as promoting noble-metal catalytic activity. The capability for storing and releasing oxygen is believed to be the result of the rapid formation and elimination of oxygen vacancy defects. Therefore, defects at slightly and strongly reduced CeO_2, specifically on the thermodynamically most stable (111) surfaces are of great interest as they may be the key to understanding surface chemistry on ceria.

To reveal and identify surface and sub-surface defects on $CeO_2(111)$, we apply dynamic scanning force microscopy (NC-AFM) providing highest resolution images of the surface structure and its irregularities. For the identification of defects, the detailed atomic structures of features found in experiments is related to predictions from DFT calculations on relevant surface defects. In this way, we are able to identify surface and sub-surface vacancies, surface hydroxide and Ce^{3+} ions. Furthermore, we demonstrate that water readily adsorbs at the surface at room temperature but may diffuse and cluster on terraces as well as step edges. Individual water molecules can also be laterally manipulated by the tip of the force microscope with atomic precision.

10:40am NS-ThM9 High-Resolution Atomic Force Microscopy in Three Dimensions

U.D. Schwarz*, M.Z. Baykara, T.C. Schwendemann, B.J. Albers, N. Pilet, E.I. Altman*, Yale University

With the recent introduction of three-dimensional atomic force microscopy (3D-AFM), the recording of dense three-dimensional surface force and energy fields with atomic resolution have become possible for the first time [1]. The main obstacles for producing high-quality 3D force maps are long acquisition times that lead to data sets distorted by drift, and tip changes. Both problems are reduced but not eliminated by low-temperature operation.

As we will show, key for the successful realization of 3D-AFM is the application of novel data acquisition and analysis procedures. In particular, an image-by-image data acquisition scheme cuts measurement times by avoiding repeated recording of redundant information, while allowing post-acquisition drift correction. All steps are illustrated with measurements performed on highly oriented pyrolytic graphite in ultrahigh vacuum at a temperature of 6 K. The area covered spans several unit cells laterally and vertically from the attractive region to where no force could be measured. The resulting fine data mesh maps piconewton forces with 6.8 pm lateral and 2 pm vertical resolution. From this 3D data set, two-dimensional cuts along any plane can be plotted. Cuts in a plane parallel to the sample surface show atomic resolution, while cuts along the surface normal visualize how the attractive atomic force fields extend into vacuum. At the same time, maps of the tip-sample potential energy, the lateral tip-sample forces, as well as the energy dissipated during cantilever oscillation can be produced with identical resolution (pN resolution for forces, meV for energies, pm for x, y, and z). Room temperature operation might be possible due to the unique post-acquisition drift correction ability. Applications in the areas of chemical imaging, surface catalysis, nanotribology, thin film growth, and device fabrication are envisioned.

[1] B. J. Albers *et al.*, Nature Nanotechnology **4**, 307 (2009).

11:00am NS-ThM10 Looking Deeper: Multifunctional Scanning Probe Microscopy

I. Riisness, R. Ramos, C. Carach, ***M. Gordon***, University of California Santa Barbara

Scanning probe microscopy (SPM) has truly revolutionized the morphological and electrical characterization of surfaces at the nanoscale; however, it is still impossible to identify and image the chemical functionality of a surface at similar resolutions. For the latter, one desires a hybrid probe system which combines traditional SPM functionality with spatially-correlated spectroscopic (chemical) data at length scales <10 nm.

To this end, we will highlight multifunctional surface imaging of chemistry, morphology, and elastic/electrical properties for several material systems using our hybrid SPM instrument. In this system, a plasmonically-active metallic tip is used to locally enhance EM fields in the tip-surface gap, enabling near-field chemical imaging via Raman spectroscopy. In this talk, we will discuss instrument design, tip preparation/characterization, and initial imaging results on polythiophene-based photovoltaic films, phase-segregated diblock co-polymers, and adsorbates on metallic nanoparticles.

Plasma Science and Technology
Room: A1 - Session PS1-ThM

Applications of Plasma-Surface Interactions
Moderator: L. Stafford, Université de Montréal, Canada

8:00am **PS1-ThM1 Coupled Ion, Photon and Electron Synergies in Plasma-Surface Interactions for Organic Materials**, ***D.B. Graves***, University of California at Berkeley

Recent experimental and simulation studies have revealed that plasma-organic surface chemistry can be strongly affected by synergistic interactions among ions, vacuum ultraviolet (VUV) photons and electrons at surfaces. In this talk, I summarize our recent studies of these synergies, focusing on various polymer and SiCOH low-k dielectric materials. When plasma and vacuum beam measurements, coupled with molecular dynamics (MD) simulations, are compared for various materials and various exposure conditions, certain patterns emerge. MD shows that (~ 100 eV) ion effects are restricted to several nm near the surface, but that their effects can depend strongly on the type of polymer and other species present. The synergistic effects of plasma-generated ions, photons and electrons can be understood in terms of a competition between bond-breaking scissioning reactions and bond-forming cross-linking and other reactions. The complexity of the results is due in part to the fact that these species have different depths of penetration, and that their bond breaking and bond forming reactions depend on the structure of the material. However, even greater complexity results from the fluence- or dose-dependent nature of electrons and ions: low dose result in scissioning and higher doses result in cross-linking. The effects of simultaneous exposure depend on both position relative to the surface and time. I illustrate these ideas with examples taken from PMMA-based 193 nm photoresists; poly-alpha methyl styrene (PaMS) and poly-four methyl styrene (P4MS); and ultra low k, nanoporous SiCOH. MD simulations and models of VUV photon penetration into polymers are used to interpret both plasma and vacuum beam experimental results.

8:20am **PS1-ThM2 Control of Photoresist Erosion in SiO_2 Plasma Etching in DC Augmented CCP Tools**, ***M. Wang***, Iowa State University, *M.J. Kushner*, University of Michigan

Polymer photoresists are commonly used for pattern transferring in plasma etching of sub-0.1 micron features in microelectronics fabrication. Degradation and erosion of the photoresist (PR) is a major issue in controlling feature profiles, especially for high aspect ratio (HAR) features where etch times are long. For example, during fluorine based plasma etching of SiO_2, erosion of the photoresist leads to bowing of the top of the profile as the etch proceeds. Multilayer masking is one approach to minimize these effects. By depositing a hard mask layer under the PR, the pattern is transferred to the hard mask layer before the PR is eroded away. Another promising strategy is to deposit a hard mask layer onto the PR surface during the process. This can be achieved in-situ by low energy ion bombardment of the PR surface to both promote cross-linking and produce dangling bonds, coincident to there being a flux of Si radicals. The resulting Si-C bonding provides a hard-mask like surface. Another is to promote fluorocarbon deposition on the PR mask to slow its erosion. These opportunities may be afforded by dc-augmented capacitively coupled plasmas (CCPs) in which the silicon covered dc electrode is sputtered. In this talk, we discuss scaling laws for profile and PR control derived from a computational investigation of a dc augmented single/dual frequency CCP reactor to generate an $Ar/C_4F_8/O_2$ plasma and fluxes of Si radicals by sputtering the dc electrode. Fluxes (energy and angle resolved) of ions, radicals and electrons are obtained from the Hybrid Plasma Equipment Model (HPEM) as a function of dc voltages, rf frequencies and rf bias powers. Profiles of features are then simulated by the Monte Carlo Feature Profile Model (MCFPM). Both multilayer mask and Si deposition strategies will be discussed. Etching selectivity between SiO_2 and mask material and feature profiles will be discussed as functions of Si fluxes, initial patterns and thickness of the photoresist.

*Work supported by Tokyo Electron Ltd., and the Semiconductor Research Corp.

8:40am **PS1-ThM3 Ultimate Top-down Processes for Future Nanoscale Devices - Novel Neutral Beam Process and Control of Atomic Layer Chemical Reaction**, ***S. Samukawa***, Tohoku University, Japan **INVITED**

For the past 30 years, plasma etching technology has led in the efforts to shrink the pattern size of ultralarge-scale integrated (ULSI) devices. However, inherent problems in the plasma etching, such as charge build-up and UV photon radiation, limit the etching performance for nanoscale devices. To overcome these problems and fabricate sub-10nm devices in practice, neutral-beam process has been proposed. In this paper, I introduce the ultimate etching processes using neutral-beam sources and discuss the fusion of top-down and bottom-up processing for future nanoscale devices. Neutral beams can perform atomically damage-free etching and surface modification of inorganic and organic materials. Namely, the neutral beam process can precisely control the atomic layer chemical reaction and defect generation. This technique is a promising candidate for the practical fabrication technology for future nanoscale devices.

9:20am **PS1-ThM5 Accurate Control of Ion Bombardment in an Expanding Thermal Plasmas**, ***P. Kudlacek***, *R.F. Rumphorst, A. Illiberi, M.C.M. van de Sanden*, Technical University Eindhoven, The Netherlands

Remote plasmas are extensively used in industry for both etching and deposition of materials. As ion bombardment has been found to be crucial for controlling deposited material properties or enhancing etch rate and anisotropy during ion induced etching, an additional bias voltage is often applied to the substrate to control the energy of the bombarding ions and/or enlarge their flux onto the substrate. Recently, a pulsed bias scheme became subject of increased interest as a promising technique to reach narrow, almost mono-energetic ion energy distribution (IED) when dielectric substrates are being processed, especially considering that the conventionally used radio frequency bias inherently leads to a bimodal IED. Moreover it offers an ultimate control of the ion flux onto the substrate by varying the duty cycle.

Experiments were run in a remote expanding thermal plasma (ETP) reactor, in Ar and Ar/H_2 gas mixture compositions. The substrate holder was negatively biased (up to -100V) by means of a home designed pulsed power supply operating with a frequency up to 200 kHz and a variable duty cycle. Ion energy distributions have been measured by means of a planar gridded retarding field energy analyzer.

Two pulsed biasing approaches will be presented (asymmetric rectangular pulses and modulated pulses with a linear voltage slope during the pulse) and their applicability is discussed on the basis of an intrinsic capacitance of the processed substrate-layer system. The substrate voltage and current waveforms were measured and mutual relations with the obtained ion energy distributions will be shown for both aforementioned cases. To demonstrate the IED control achieved, the effective carrier lifetime of n-type c-Si wafers, passivated by an a-Si:H thin film, as a function of the flux and energy of bombarding argon ions was determined. The ion energy and ion flux was independently varied and threshold ion bombardment characteristics leading to degradation of the effective lifetime will be presented.

9:40am **PS1-ThM6 Plasma Induced Modification of an Organic Photoconductor in an Electrophotographic System**, *K. Nauka*, ***S. Chang***, *H.-T. Ng*, Hewlett-Packard Company

The goal of this study was to elucidate structural and compositional modifications of an organic photoconductor after an extensive exposure to plasma discharge by a charging element within an electrophotographic system. An organic photoconductor, commonly found in a variety of applications ranging from simple copiers to advanced high-speed digital presses, is the key element of the modern electrophotographic printing system. It facilitates formation of the latent image resulting from the area-selective light discharge of uniformly distributed charges deposited on its surface by the plasma. Its undesirable modifications may adversely impact the print quality.

Modifications of the photoconductor's surface layer were investigated with the help of Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy (ATR) and X-ray Photoelectron Spectroscopy (XPS). The experimental set-up was designed to simulate interactions between the plasma discharge and photoconductor occurring in a typical electrophotographic printing environment. Experiments were performed over an extended period of time corresponding to printing multiple pages. UV radiation and energetic particle bombardment originating from the plasma are the two major processes responsible for the photoconductor modifications. Therefore, further elucidation of the photoconductor modification phenomenon was obtained by employing the UV-only and the particle bombardment-only experimental conditions.

A long time exposure of the photoconductor to energetic neutral and charged species, and UV photons caused massive oxidation, substantial chemical bond breakage, and reformation of bonding configuration within a thin layer below the surface. This layer can be divided into two regions corresponding to the aforementioned photoconductor modification processes. The top region, having thickness of approximately 20nm - 30 nm, is formed primarily by the particle bombardment. It is heavily oxidized and its thickness is limited by the bombardment induced sputtering. Thicker region below is relatively free of oxygen and its molecular composition is distinctly different from the original photoconductor. It is primarily formed by UV-induced cracking of the benzene rings followed by reformation of the excited radicals into new molecular species. Thickness of this region corresponds to the UV penetration depth. The possibility of preventing the formation of a parasitic surface layer will be further discussed.

10:40am **PS1-ThM9 Control of Selectivity and Profile for HfO_2 Etching in BCl_3-Containing Plasmas**, ***K. Nakamura***, *Y. Ueda, H. Kiyokami, H. Tsuda, K. Eriguchi, K. Ono*, Kyoto University, Japan

Selective etching of high dielectric constant (high-*k*) films over the underlying Si (and/or SiO_2) is indispensable in the fabrication of high-*k* gate stacks. In practice, the selectivity is usually not so high, owing to highly volatile halogen compounds of Si, and also to strong metal-oxygen bonds of high-*k* dielectrics and less volatile metal-halogen compounds. Profile control is also indispensable during etching of high-*k*: anisotropic profiles are required for high-*k*, and also profiles of gate electrodes on high-*k* are required to remain unchanged. This paper presents the control of selectivity and profile for high-*k* HfO_2 etching under low ion-energy conditions in BCl_3-containing plasmas, with emphasis being placed on a better understanding of the etching mechanisms concerned. Experiments were performed in both electron cyclotron resonance (ECR) and inductively coupled (ICP) plasmas, by varying pressure, additive concentration of O_2, Cl_2, and Ar, rf bias power, and also substrate temperature. Samples for etching were blanket HfO_2 and TaN films, and separate Si and SiO_2 substrates were also employed for reference. Samples of TaN/HfO_2 stack as well as separate HfO_2 and TaN masked with line-and-space patterns were also employed to examine the etched profile. We examined substrate surfaces by x-ray photoelectron spectroscopy, and investigated reactant and product species in the plasma during etching by optical emission spectroscopy and quadrupole mass spectrometry. A transition from deposition to etching regimes was found to be caused on all substrate surfaces, by varying pressure, by using additives such as O_2 and Cl_2, and by increasing rf bias power. In practice, surface inhibitor deposition was less significant for HfO_2 than for Si, SiO_2, and TaN; and the threshold bias power or ion energy for HfO_2 etching was in the range 10-20 eV, while the threshold was more than 20 eV for the other. A difference in pressure, additive concentration, and bias power for the transition between HfO_2 and Si (and/or SiO_2) gave rise to high or infinite selectivity of high-*k* over Si (and/or SiO_2), together with vertical high-*k* profiles. The difference for the transition between HfO_2 and TaN also gave no significant distortion of TaN profiles during HfO_2 etching, owing to passivation layers deposited on TaN sidewalls. Plasma and surface diagnostics indicated that inhibitor species for deposition are primarily boron-chloride polymers produced in the plasma, whose concentration largely depends on pressure, additive concentration, and plasma reactor (ECR and ICP), which in turn leads to a marked difference in etching characteristics.

11:00am **PS1-ThM10 Etching Mechanisms of FeCo Magnetic Films by Chemically Reactive Energetic Ion Injections**, ***K. Karahashi***, *T. Ito, Y. Matsumoto, S. Hamaguchi*, Osaka University, Japan

Reactive ion etching (RIE) has been widely used for semiconductor micro fabrication processes. Recently magnetic thin films have also become materials of choice for some specific microelectronics applications such as magnetic random access memory (MRAM) and read/write heads for magnetic data storage. For micro fabrication processes of magnetic films, Ar ion milling seems to be almost the only etching technique in the current manufacturing processes. However, capabilities of Ar ion milling for anisotropic and selective etching of magnetic films are severely limited and therefore new technologies of reactive ion etching for magnetic films are now seriously sought. In this study, we have focused on etching processes of FeCo alloy thin films and examined their surface reactions caused by energetic Cl+ ion beam injections. More specifically we have measured desorbed products and etching yields (i.e., sputtering yields) of the sample, using a mass-selected ion beam system. The ion beam system can inject mono-energetic single-species ions (i.e., Cl+ or Ar ions in this study) to the sample (i.e., FeCo, Fe, or Co thin film) surface in ultra-high vacuum conditions. The reaction chamber, where the sample is placed, is equipped with a quadrupole mass spectrometer (QMS), a temperature programmed desorption (TPD) system, and an X-ray photoelectron spectroscopy (XPS). The QMS is used for the detection of desorbed products during the ion beam injections and XPS is used for in-situ chemical analyses of irradiated surfaces. The Cl+ ion beams used in this study are in the range of 250-1000eV. The etching yields are determined from measured depth profiles of irradiated surfaces and ion fluxes. It has been found that the etching yields of FeCo and Fe films by Cl+ ion injections below 300 eV are smaller than those of Co films under the same conditions. It has been also found that iron chlorides (FeClx) are formed on Fe surfaces under Cl+ ion injections and their amounts increase with the increasing Cl+ ion dose. These results indicate that the reduction of etching rate of FeCo below 500eV is caused by the formation of FeClx on the surface. TPD of volatile materials from Cl+ injected Fe surfaces has shown that FeClx desorbs when the surface temperature is above 600K. This suggests that the control of substrate temperature is crucial for Cl-based reactive ion etching of FeCo. We have also compared these results with physical sputtering characteristics of FeCo films by energetic Ar injections.

11:20am **PS1-ThM11 Characterizing the Effects of Etch-Induced Material Modification on the Crystallization Properties of Nitrogen Doped $Ge_2Sb_2Te_5$**, *E.A. Joseph, S. Raoux, J.L. Jordan-Sweet,* IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr*, D. Miller, H.-Y. Cheng,* IBM/Macronix PCRAM Joint Project - IBM Almaden Res. Ctr*, A. Schrott, C.-F. Chen, R.K. Dasaka,* IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr*, R.M. Shelby,* IBM/Macronix PCRAM Joint Project - IBM Almaden Res. Ctr*, Y. Zhang,* IBM/Macronix PCRAM Joint Project - IBM T.J. Watson Res. Ctr*,* ***J.S. Washington****, M.A. Paesler, G. Lucovsky*, North Carolina State Univ.

Chalcogenide-based phase change memory devices have recently garnered significant interest due to their potential scalability beyond that of conventional DRAM and Flash memory technologies.[1] Due to the stringent demands imposed by the scaling roadmap, it is becoming increasingly important to understand the effects of processing on the crystallization properties of the material since it is known that there is an etch-induced material modification layer resulting from patterning.[2] In this work, we examine chemical and structural effects of processing on the crystallization properties of nitrogen doped Ge2Sb2Te5 using X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), time resolved laser reflectivity and time resolved X-ray diffraction (XRD). The laser reflectivity results indicate that upon exposure to various etch and ash chemistries the (re)crystallization speed is significantly reduced. Time resolved XRD data further show that the transition temperature from the rocksalt to the hexagonal phase is increased from 400 ºC to ~ 500 ºC. From depth profiled XPS and XAS measurements, we attribute this increase in crystallization time (and increase in transition temperature) to the selective removal and/or oxidization of numerous elemental species (N, Ge, Sb, Te) which alters the local bonding environment and which may result in the formation of additional phases. The relevance of these effects and their ability to potentially alter device performance will also be discussed.

[1] Y.C. Chen, C.T. Rettner, S. Raoux *et al.*, IEDM Tech. Dig., p. S30P3, 2006.

[2] E. A. Joseph, T. D. Happ, S.-H. Chen, S. Raoux, et al., Symp. VLSI-Technology Systems and Applications, 2008. pg 142-143, 2008

11:40am **PS1-ThM12 Surface Properties of Plasma Treated Metal Oxides**, ***K. Trevino***, *E.R. Fisher*, Colorado State University

Metal oxides are used for various applications including polymer adhesion, anticorrosive coatings, and catalysis. Plasma treatments have proven useful in tailoring the properties of such surfaces due to their ease of use and environmental friendliness. However, the interfacial interactions that give rise to changes in surface charge and acid/base character are poorly understood. Measurement of these properties, along with surface characterization, allows for a clearer understanding of the important chemical processes. Of particular concern is the permanency of the surface treatment, which is expected to depend on plasma type, plasma conditions, substrate, and the position of the substrate in the plasma. In this work, we have separately treated SiOxNy surfaces with three non-polymerizing gases (Ar, H_2O, and NH_3) and monitored surface properties as a function of plasma parameters and substrate position for a period of thirty days. Surface charge and acid/base character were measured by determination of the isoelectric point (IEP) from contact angle titration data; surface composition and morphology were also taken and analyzed by XPS and SEM. Ar-plasma treatments yielded initial IEP values of ~7, however these values are not stable over time. In contrast, IEP values for H_2O plasma treatments also increased (compared to an untreated substrate) to ~6, but stay relatively stable with age. Compositional data reveal information about the effectiveness of the treatments, and IEP data highlight the similarities and differences between the plasma systems. Results from additional metal oxides and polymer surfaces will also be presented and comparisons between systems will be made.

Plasma Science and Technology
Room: B2 - Session PS2-ThM

Plasma Sources
Moderator: J.-P. Booth, CNRS/Ecole Polytechnique, France

8:00am **PS2-ThM1 Power Dynamics in Low Pressure Capacitively Coupled Plasma Discharges**, ***S. Rauf***, *K. Bera*, *L. Dorf*, *K. Collins*, Applied Materials, Inc.

As feature sizes shrink and feature aspect ratios increase in advanced microelectronics devices, critical dielectric etching processes in capacitively coupled plasmas (CCP) are generally transitioning towards lower gas pressures (< 30 mTorr). Long electron mean free path and large bias voltages in this regime means that kinetic effects play an important role in the power dynamics in these low pressure plasma discharges. A coupled one-dimensional particle-in-cell (PIC) and fluid model is used to understand power dynamics in low pressure CCP discharges in this investigation. Our PIC model for charged species is based on the well-established computational techniques developed by Birdsall and colleagues (C. K. Birdsall and A. B. Langdon, *Plasma Physics via Computer Simulation*, IOP Publishing, Bristol, 1991) and includes a Monte Carlo based model for charged species collisions. Since multiple neutral species are present in plasmas of typical etching gases, the PIC model is coupled to a fluid model for neutral species that takes into account species transport in the plasma bulk, chemical reactions, and surface processes. The PIC + fluid model is applied to understanding power dynamics in a variety of etching-relevant single and dual frequency plasmas including Ar, O_2, and CF_4. Substantial fraction of applied power is consumed by the ions in the sheaths, which is dissipated at the electrodes. In Ar, electrons primarily gain energy at the sheath edge during sheath expansion, which results in highly energetic electrons. These energetic electrons stream through the plasma towards the opposite electrode, causing excitation, dissociation and ionization in their path. At low pressures (< 50 mTorr), these energetic electrons are able to reach the opposite sheath and lose some their energy while decelerating in the sheath. This behavior is consistent with the fact that plasma density is lower at lower pressure in the 5 – 50 mT range. The situation becomes more complicated in molecular gases due to electron collision processes with low threshold energies. Secondary electrons play an important role in sustaining the plasma at low frequencies (< 30 MHz), but sheath heating of electrons is sufficient for plasma sustenance at higher frequencies (> 60 MHz). Simulation results will be compared to experimentally measured ion densities.

8:20am **PS2-ThM2 Ballistic Electrons and Resulting EED*f* in a DC+RF Hybrid CCP Reactor**, ***L. Xu***, *L. Chen, M. Funk*, Tokyo Electron America

The DC+RF Hybrid is a capacitively coupled plasma (CCP) etcher with RF applied to the wafer electrode and a high-negative DC voltage on the opposite electrode 3cm away. Ion-secondary-electrons from the DC electrode are accelerated by the DC-sheath into the plasma as ballistic electrons. Gridded energy analyzers are placed behind the RF electrode for EED*f* measurements. Experiment's pressure-range varies from 30 mTorr to 70 mTorr with DC-voltage up to –1kV. EED*f* reveals, (1) Maxwellian bulk, (2) ballistic electrons with energy corresponding to the applied DC-voltage, (3) a continuum from Maxwellian to the ballistic electron peak, (4) middle-energy electrons with distinct energy-peak. Measured EED*f* qualitatively agree with PIC numerical experiment. The energy of the distinct middle-energy peak seems to depend on the sheath thickness and varies from ~ 40eV to 300eV. While ballistic electrons' finite collisions contribute to the continuum, other non-negligible channel such as Landau-damped e^--beam plasma waves, should be considered. The distinct middle-energy peak could result from Landau damping of a strong plasma wave of a specific wave number. The energy range of middle-energy peak is favorable in sustaining ionization, rendering the necessity of heating the Maxwellian bulk for a similar level of ionization.

8:40am **PS2-ThM3 Simulation of 450 mm Dual Freqeuncy Capacitively Coupled Plasma Tools: Conventional and Segmented Electrodes**, ***Y. Yang****, Iowa State University, *M.J. Kushner*, University of Michigan

Wafer diameters will soon transition from 300 mm to 450 mm at a time when excitation frequencies for capacitively coupled plasmas (CCPs) are increasing to 200 MHz or higher. Already for 300 mm tools, there is evidence that wave effects (i.e., propagation, constructive and destructive interference) affect the processing uniformity. The increase to 450 mm is likely to exacerbate these affects, perhaps requiring non-traditional tool designs. This is particularly important in dual frequency (DF) CCP tools in which there are potential interactions between frequencies. In this talk, we discuss results from a 2-dimensional modeling study of the plasma properties in 450 mm DF-CCP tools. To resolve wave and electrostatic effects, a full-wave Maxwell equation solver in the Hybrid Plasma Equipment Model is employed. To capture the high frequency heating, excitation rates are provided by spatially dependent electron energy distributions generated by a Monte Carlo simulation. A Monte Carlo simulation is also used to predict ion energy distributions as a function of radius on the substrate. Results will be discussed for plasma properties in DF-CCPs for low frequencies of ≤ 10 MHz and high frequencies up to 200 MHz, and gas pressures of < 10s mTorr. Segmented electrodes will be discussed as a means to suppress wave effects by making the electrical distance between the electrode feeds and the sheath edges as uniform as possible. The effects of tuning the lengths of the segments and the positions of rf feeds on plasma uniformity will be discussed.

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

9:00am **PS2-ThM4 A Scalable, VHF/UHF Compatible, Capacitively Coupled Plasma Source for Processing Large-Area Substrates at High Frequencies**, ***A.R. Ellingboe***, *D. O'Farrell, C. Gaman,* Dublin City University, Ireland*, F. Green, N. O'Hara, T. Michna*, Phive Plasma Technologies, Ireland

A recent trend in plasma etching and plasma enhanced CVD has been the increase in rf frequency used to sustain the plasma. For capacitively coupled plasma sources, increasing the rf frequency increases the fraction of power coupled into the electrons in comparison to ion energy gained in the sheath. The concept of 'high-frequency chemistry' is discussed, and some evidence that systems operated at hundreds of Megahertz have different electron kinetics have been presented (Samukawa, etal, J. Vac. Sci. Technol. A 17(5), Sep/Oct 1999, and D.O'Farrell, this conference).

However, the present trend to increase rf frequency is incompatible with increases in wafer size to 450mm and beyond.

No where is the evidence more clear than in PECVD of amorphous and microcrystalline Silicon for the photo-active layer in thin-film photovoltaic devices. Growth rates for these layers, while maintaining the necessary mechanical and electrical properties, can increase with increasing rf frequency, and in some cases yield superior film properties at the higher deposition rates (P.G. Hugger, etal, MRS 2008). However, in this industry substrate sizes are very large, exceeding 1m characteristic lengths, which puts substantial limits for a conventional plasma diode topology on using frequency as a control vector to increase deposition rate, thus increasing factory through-put and decreasing cost.

In this talk we will introduce a novel plasma source topology that enables increased rf frequencies on arbitrary size plasma source without causing wavelength effects. The concept is to segment the powered electrode into discrete tiles; For example as a checkerboard. Adjacent tiles can be powered out of phase with each other. In this way the displacement current coupled by one electrode is balance by and equal and opposite current of the adjacent electrode. Thus zero net current is coupled into the plasma, zero net current is coupled through the sheath above the substrate, and no wavelength effects occur even for substrates large in comparison to the rf wavelength.

Highlights of recent results in the operation and application of the plasma source to PECVD of silicon will be presented.

9:20am **PS2-ThM5 Characteristics of Ferrite Enhanced Internal Linear Antenna for Large Area (2750mm x 2350mm) Inductively Coupled Plasma Source**, ***J.H. Lim***, *K.N. Kim, G.H. Gweon, S.P. Hong, G.Y. Yeom*, Sungkyunkwan University, Korea

Inductively coupled plasmas sources (ICPs) have been applied to a variety of plasma processing including flat panel display processing (FPD) and semiconductor processing. Especially, for the FPD applications, to increase the inductive coupling to the plasma, internal-type antennas have been more intensively investigated.

In this study, the plasma characteristics of an internal-type linear ICP source having the size of 2750mm χ 2350mm installed with a Ni-Zn ferrite module was investigated. Especially, the effect of the Ni-Zn ferrite and different driving frequency of 2MHz and 13.56MHz on the plasma characteristics and electrical characteristics of the plasma source was investigated.

The results showed that, by the magnetic field enhancement using the ferrite, the operation of the antenna at 2MHz showed higher power transfer efficiency, lower antenna impedance, and lower rf rms voltage compared to that operated at 13.56MHz without the ferrite. For the ferrite enhanced ICP source operated at 7kW of 2MHz rf power, high density plasmas on the

---

* PSTD Coburn-Winters Student Award Finalist

order of 2.0 x 10^{11}cm^{-3} could be obtained with 15mTorr Ar which was about two higher than that obtained for the source operated at 13.56MHz. When photoresist etch uniformity was measured by etching the phtoresist using 40mTorr Ar/O_2(7:3) mixture for the operation at 2MHz with the ferrite module, the etch uniformity of about 11% could be obtained.

9:40am **PS2-ThM6 Large-Scaled ECR Line Plasma Production by Microwave in a Narrowed Rectangular Waveguide**, ***H. Shindo***, *Y. Kimura,* Tokai University, Japan*, T. Hirao*, Kochi Institute of Technology, Japan

Long line-shaped plasmas are inevitable in material processing in manufacturing industries, such as solar cell film CVD, flat panel displays (FPDs), and various surface modification of large-area thin films. In this work, a newly proposed method of large-scaled line plasma production is studied. In particular a long line ECR (Electron Cyclotron Resonance) plasma production is examined. In this method, microwave power of frequency of 2.45 GHz in a narrowed and flattened rectangular waveguide is employed to produce a long uniform ECR line 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 line high density plasma with a great uniformity.

The narrowed rectangular wave-guide of 1.0 and 2.0 m in length and 5mm in height were prepared and the width of the waveguide is 62 mm which is very closed to the cut-off condition. The waveguide has a long slot on the top surface to launch the micro-wave into the discharge plasma chamber of 1.0 and 2.0 m in length. At the end of wave guide, a short plunger was quipped to adjust the phase of the standing microwave, hence the uniformity of the plasma thus produced. The magnetic field, which is generated by NdFeB magnet of 20 mm in thickness and 50 mm in width, is applied to plasma to produce the resonance field of 875 Gauss at the position of 10mm below the slot antenna. The plasmas of Ar at the pressures of 0.5 to 5Torr were produced by employing an extremely long microwave wavelength. The plasma thus produced was three-dimensionally measured by a Langmuir probe.

The electron density in the plasma thus produced showed a very high value, as high as 10^{12} cm^{-3} at the pressure of 0.5 Torr. In particular the cross sectional profile of the electron density showed a strong magnetic filed dependence and it becomes highest at the ECR resonance point, one order higher than in non-resonance region, indicating that the plasma production is due to the electron cyclotron resonance. The axial profile of electron density is quite good and the plasma uniformity was within 5 % in the entire plasma, indicating that the ECR line plasma is realized. It was also found that the profile of electron density was adjustable by the short plunger. To be specific, the electron density measured at a fixed Z position showed a standing wave-like profile, indicating the short plunger has a function of phase-shifter as expected. Thus we conclude that the present method of large-scaled ECR line plasma production is quite advantageous for large area processing.

10:40am **PS2-ThM9 PIC Simulations and Probe Measurements of the EEDF in a Microwave Surface-Wave Plasma Source**, ***R.V. Bravenec***, Fourth State Research, under contract to Tokyo Electron America, Inc.*, J.P. Zhao, L. Chen, M. Funk,* Tokyo Electron America, Inc.*, C.Z. Tian, K. Ishibashi, T. Nozawa*, Tokyo Electron Technology Development Institute, Japan

Microwave surface-wave plasma sources for wafer etching or deposition are promising alternatives to capacitively- or inductively-coupled sources. Unlike the latter, the source and wafer are decoupled, such that the wafer may be independently biased without affecting the source. Furthermore, microwave surface-wave sources are known to produce relatively dense, quiescent, low-temperature plasmas near the wafer surface, thereby minimizing wafer damage. Our device consists of an RLSA (radial line slot antenna) which transmits 2.45 GHz microwaves into a large quartz resonator disk which then couples to the plasma. We compare 2-D PIC (particle-in-cell) simulations from the VORPAL code[1] with Langmuir probe measurements[2] of the EEDF (electron energy distribution function) of the plasma. The simulations, a continuation of earlier work,[3] include ionization using a Monte-Carlo model with an energy-dependent cross section. Secondary emission from the quartz surface is modeled with energy and incident-angle dependent yield and produces a specific energy spectrum of outgoing particles. Fitting of the probe I-V curves employs a novel method of assuming from the outset two Maxwellian distributions plus a drifting Maxwellian to model a beam component. This method, unlike fitting the curves to polynomials or such, aids in interpretation of the results. We find that the EEDF near the resonator disk is typically dominated by the beam component, transitions to two Maxwellians away from the disk, then thermalizes to a single cold Maxwellian near the wafer surface. Simulations and data for various plasma densities and gas pressures will be presented.

[1] C. Nieter and J. R. Cary, J. Comp. Phys. **196**, 448 (2004).

[2] J. P. Zhao et al., poster at this conference

[3] R. V. Bravenec et al., poster at Gaseous Electronics Conference, Dallas, Oct., 2008.

(Research funded by Tokyo Electron Technology Development Institute. The authors also acknowledge the contributions of C. Roark, D. Smithe, and P. Stolz of Tech-X Corp.)

11:00am **PS2-ThM10 Characterization of an Expanding Chlorine Plasma Produced by an Electromagnetic Surface-Wave**, ***O. Boudreault***, *S. Mattei,* Université de Montréal, Canada*, R. Khare,* University of Houston*, L. Stafford,* Université de Montréal, Canada*, V.M. Donnelly*, University of Houston

Plasmas produced by propagating surface waves have attracted attention because of their long and stable plasma columns without accompanying guiding structures. This is because the electric field supporting the discharge is provided by a traveling wave that carries the power away from the applicator, guided by the plasma column and the dielectric tube enclosing it. In long, narrow plasmas the wave-to-plasma power transfer is usually assumed to occur locally such that the axial density profile is determined by the wave attenuation coefficient. As a result the electron density, n_e, decreases in a quasi-linear manner along the plasma column in the direction of the wave propagation down to the critical density for surface wave propagation where the plasma decays abruptly (= expansion region) . At low pressures, however, the plasma tends to expand well beyond this critical point such that the description of the axial density distribution in terms of the local approximation is no longer valid. We investigated the influence of gas pressure on the spatial structure of a high-density chlorine plasma produced in a 6 mm, inside diameter, quartz tube by a propagating 2450 MHz surface wave. The axial variation of the electron density was determined from the spatial phase characteristics of the wave and the 828.0 nm emission line of Xe inserted as a tracer. As expected, n_e decreased linearly with axial position from the wave launcher, except in an expansion region near the end of the plasma column where the decrease of n_e was more abrupt. The thickness of this expansion region decreased with increasing pressure, going from about 8 cm at 5 mTorr to less than 1 cm at 100 mTorr. The Cl_2 percent dissociation obtained from the calibrated Cl_2(306 nm)-to-Xe emission ratio remained fairly constant except in the expansion region where it decreased sharply. For example, at 5 mTorr, the Cl_2 percent dissociation was 95 % near the wave launcher and 15 % at 2 cm from the end of the plasma column. While the expansion region showed a decrease in the electron density and Cl_2 percent dissociation, no noticeable change in the electron energy distribution function (EEDF) was observed. For all pressures and axial positions, the EEDF determined by trace-rare-gas-optical-emission-spectroscopy remained Maxwellian. The electron temperature (T_e) was fairly independent of the axial position, going from ~12 eV at 5 mTorr to ~2 eV at 100 mTorr. The high T_e values are due to a combination of high gas temperatures (T_g = 463 K at 5 mTorr and 635 K at 100 mTorr, measured by N_2 C->B emission rotational spectra) and small tube bore (0.6 cm), and are in good agreement with a global model.

11:20am **PS2-ThM11 Vacuum Ultraviolet Plasma Emission in a Capacitively-Coupled Dielectric Etch Reactor**, ***E.A. Hudson***, *M. Moravej, M. Block, S. Sirard, D. Wei, K. Takeshita,* Lam Research Corp.*, B. Jinnai, S. Samukawa*, Tohoku University, Japan

Plasma optical emission in the visible and ultraviolet (UV) ranges is widely used to characterize the properties of thin-film processing plasmas. Emission in the vacuum ultraviolet (VUV) range is less commonly detected due to the challenges of eliminating air from the optical path. However the interaction of VUV radiation with the substrate may be important in plasma processing, particularly for device damage and for the modification of sensitive materials such as low-k dielectrics and 193nm photoresist. To improve the understanding of these mechanisms, a windowless optical system was incorporated onto a commercial capacitively-coupled confined-plasma dielectric etch reactor. VUV and UV emission spectra in the 40 – 230nm range were measured for a range of plasma conditions, including simple single-gas plasmas and more complex etching plasmas. The spectra showed a strong dependence on gas chemistry, due to the characteristic emission lines associated with the plasma atomic and molecular composition. More importantly, the frequency of plasma electrical excitation was found to influence the VUV spectra. Correlations were observed between plasma emission in specific wavelength ranges and process-induced low-k dielectric damage.

11:40am **PS2-ThM12 Damage-Free, Uniform and High-Target-Utilization Novel Magnetron Sputtering Plasma Source by Rotating Helical Magnet**, ***T. Goto***, Tohoku University, Japan, *N. Seki*, *T. Matsuoka,* Tokyo Electron Technology Development Institute, Inc., Japan, *T. Ohmi*, Tohoku University, Japan

Novel magnetron sputtering equipment, called rotation magnet sputtering (ROT-MS), is being developed to overcome various disadvantages of current magnetron sputtering equipment. Disadvantages include:(1) very low target utilization of less than 20%, (2) difficulty in obtaining uniform deposition on the substrate, and (3) charge-up damages and ion-bombardment-induced damages resulting from very high electron temperature and that the substrate is set at the plasma-excitation region. In ROT-MS, a number of moving high-density plasma loops are excited on the long rectangular flat target surface by rotating helical magnets, and the deposition is performed by passing the substrate through this deposition region, resulting in very high target utilization with uniform target erosion and uniform deposition on the substrate due to time-averaging effect. T his excellent performance can be principally maintained even as equipment size increases for very large-substrate deposition. Plasma characteristics and deposition performances were investigated using ROT-MS equipment for both 8-inch wafer and 200-mm-square substrate. Deposition uniformity on 8-inch wafers for pure Al deposition results in that the film-thickness uniformity (defined by standard deviation divided by average thickness) is 0.5～2.5% in the wide pressure range from 0.33 to 5.3 Pa for the cases without any optimization of slit width configuration. The target utilization is estimated to be 59.7% from the measurement of the target erosion distribution. It is found that the target erosion distribution experimentally observed agrees well with the theoretical calculation. We have calculated target utilization for various helical magnet configurations, and revealed that very high target utilization larger than 90% is feasible. Detailed ion current distributions at the substrate were measured by measuring ion saturation currents flowing to the multipoint probes set at the stage (in this measurement, the helical magnet is not rotating). The results show that the distribution is uniform within the slit area for the rf-excited plasma case with the order of 1 mA/cm^2, while the distribution of the magnetic filed loop pattern is observed with the order of 0.1 mA/cm^2 for the dc-excited case. Because strong horizontal magnetic fields (>0.05 T) are produced within a very limited region just at the target surface, very low electron-temperature plasmas (< 2.5 eV for Ar plasma, and < 1 eV for direct-current-excited Xe plasma) are excited at the very limited region adjacent to the target surface for charge-up damage-free and ion-bombardment-induced damage-free processes.

Surface Science
Room: M - Session SS1+AS+TF-ThM

Surface Science of Hazardous Materials
Moderator: V. Grassian, University of Iowa

8:00am **SS1+AS+TF-ThM1 Interactions of Nerve Agents with Model Surfaces: Computational Approach**, ***J.R. Leszczynski***, Jackson State University **INVITED**

The talk summarizes the results of recent studies performed by our group. They include modeling of interactions of selected nerve agents with model surfaces. Among studies nerve agents are soman, sarin, tabun and their surrogates. We investigated different types of surfaces: metals, metal oxides and clays. The study was performed using various techniques of non-empirical, ab inito methods. Among predicted characteristics are molecular geometries of resulting complexes, their interaction energies, electrostatic potentials, and IR spectra. We identified the most promised surfaces that facilitate decomposition of the selected nerve agents. Also, predicted differences between selected processes for nerve agents and their simulants will be discussed.

8:40am **SS1+AS+TF-ThM3 *Ab-Initio* Computational Approaches to the Adsorption of Chemical Warfare Agents**, ***V. Bermudez***, Naval Research Laboratory

Computational chemistry can be used to great advantage in dealing with chemical warfare agents (CWAs). Computation can be applied to reagents which are much too dangerous for routine experimentation as well as to non-traditional species which have not yet been (but could be) synthesized. Examples will be given from recent work[1] on the interaction of the simulant dimethyl methyphosphonate (DMMP) and the real CWAs Sarin and VX with γ-Al_2O_3 surfaces. The γ-Al_2O_3 surface acts as a Lewis acid (electron acceptor) when OH-free and a Brønsted acid (proton donor) when hydroxylated. Thus γ-Al_2O_3 is an excellent prototype for a wide range of other metal oxides. DMMP, Sarin and VX all adsorb in the same way and with a similar adsorption energy (ΔE_{ads}) which depends strongly on surface acidity. A coordinatively-unsaturated tetrahedral Al(T_d) site, which is a strong Lewis acid, forms an Al---O=P dative bond to the phosphonyl group. This is always the most favorable site, and an agent adsorbed by hydrogen bonding at an OH site will migrate to a bare Al(T_d) site if one is available. The γ-Al_2O_3 lowest unoccupied orbital is a surface state associated with the Al(T_d) site which lies just below the conduction band minimum. The energy of this state relative to vacuum is a quantitative measure of Lewis acidity and is directly reflected in ΔE_{ads}. The highest occupied orbital of the molecule is a non-bonding orbital on the phosphonyl O atom. The one-electron energy of this orbital also directly affects ΔE_{ads}. The hydroxylated surface forms Type I, II and III OH sites with O bonded to one, two or three Al's respectively. Brønsted acidity, and ΔE_{ads} for OH---O=P bond formation, increase in the order I<II<III with the Type I interaction being almost negligible. The amine group in VX is found to be a strong base, capable of deprotonating an acidic Type III OH site to form an ammonium ion even in the absence of a polar solvent. The electronic excitations of DMMP, Sarin and VX have also been investigated with the goal of identifying possible photochemical effects due to terrestrial solar radiation (TSR). This issue has been largely overlooked in previous agent-fate studies. DMMP and Sarin are insensitive at energies below ~7 eV; however, vapor-phase VX can be excited near 4.3 eV which is at the upper end of the TSR. The excitation threshold changes slightly for adsorbed VX, shifting to the red or to the blue depending on the nature of the surface. These results provide a predictive framework for understanding the effects of surface condition on the adsorption of VX and G-series CWAs on oxide surfaces.

(1) Supported by the Defense Threat Reduction Agency (DTRA)

9:00am **SS1+AS+TF-ThM4 Computational Prediction of Physical Properties and Environmental Reactivity of Nitro-aromatic and Hydrogen Reach Explosives**, ***L.G. Gorb***, *F.C. Hill,* SpecPro, Inc., *E.N. Muratov, A.G. Artemenko,* A.V. Bogatsky Physical-Chemical Institute, Ukraine, *Y.I. Kholod,* Jackson State University, *V.E. Kuz'min,* A.V. Bogatsky Physical-Chemical Institute, Ukraine, *J.R. Leszczynski*, Jackson State University

Prediction of chemical and physical properties of explosives and products of their environmental degradation, instead of expensive and toxic chemical experiments, is a very important task from many points of view. Among them water solubility (SW) is an extremely important property of chemical compounds. It plays a major role in definition of migration and ultimate fate of chemicals in the environment. In particular, high solubility leads to expeditious distribution in water, i.e., chemicals that rapidly and completely dissolve in water will be transported along with the general flow of water. High SW is generally associated with a very low affinity for adsorption to solids in water, e.g., soil particles or sediment. In addition, high water solubility is associated with accumulation of contaminants in living organisms.

Water solubility values for twenty seven nitro-apomatic and hydrogen reach compounds with experimentally measured values were computed using the conductor-like screening model for real solvent (COSMO-RS) based on the density functional theory and COSMO technique. We have found that the accuracy of the COSMO-RS approach for prediction of water solubility of liquid nitro compounds is impressively high (the errors are lower than 0.1 LU). However, for some solid nitro compounds, especially nitramines, there is sufficient disagreement between calculated and experimental values. In order to increase the accuracy of predictions the quantitative structure–property relationship (QSPR) part of the COSMO-RS approach has been modified. The solubility values calculated by the modified COSMO-RS method have shown much better agreement with the experimental values (the mean absolute errors are lower than 0.5 LU). Furthermore, this technique has been used for prediction of water solubility for an expanded set of twenty three nitro compounds including nitroaromatic, nitramines, nitroanisoles, nitrogen rich compounds and some their nitroso and amino derivatives with unknown experimental values.

Finally, an application of COSMO-RS approximation to the prediction of environmental reactivity for hydrogen reach explosives (alkali hydrolysis in water) has been briefly discussed

9:20am **SS1+AS+TF-ThM5 A Material Approach to Enable Detection of Toxic Chemicals in Water by IR Spectroscopy**, ***C.P. Tripp***, University of Maine **INVITED**

We are currently developing a detection system based on the principles of infrared (IR) spectroscopy that operates in heterogeneous aqueous environments and provides fast detection (< 10 min) and high sensitivity to chemical warfare agents and other toxic chemicals with minimal false alarms. The key enablers to using infrared spectroscopy for aqueous based detection are the development of materials that lead to selective and robust sampling protocols. In this talk, I will present new sampling methods that are based on the use of surface functionalized adsorbents and reactive thin films coated onto a porous and IR amenable support. The coatings chemically react with a predefined class of compounds and identification of the specific chemical is provided by IR spectral analysis. Examples of this approach for low level detection of cyanide, metals, pesticides, and chemical warfare agents in water will be demonstrated.

10:40am **SS1+AS+TF-ThM9 Surface Science and its Application to Energetic Materials**, ***V.J. Bellitto***, *J.M. Kelley, D.N. Sorensen*, Naval Surface Warfare Center

Composite explosives and propellants are heterogeneous admixtures of crystalline powders in a rubbery binder. Materials such as aluminum are added to enhance specific performance criteria. The aluminum although improving performance in systems may not be efficiently consumed. Placement of explosives and propellants in closer proximity with the metal is expected to provide performance enhancements. The novel material should have more complete combustion and faster energy release rates as problems with heat transfer and diffusion rates are overcome.

We have undertaken a research effort to gain a fundamental understanding of the metal/explosive interaction. In performing experiments novel interfaces are produced which are not obtainable under ambient conditions. The research reveals possible avenues for the development of new energetic materials with improved performance.

In this work, X-ray photoelectron spectroscopy (XPS) was used to study the interaction of aluminum with cyclotrimethylenetrinitramine (RDX) and the resultant products analyzed via Differential Scanning Calorimetry (DSC). For RDX, the spectrum of the N 1s region has two easily discernable peaks assigned to the nitro group and ring structure nitrogen. Upon the initial interaction of aluminum with RDX, the N 1s spectrum reveals that the nitrogen peak associated with the nitro group is diminished compared to that of the ring structure. This is an indication of the preferential reaction of the nitro group with the aluminum, leaving the ring structure intact. The data also shows the preferential formation of aluminum oxide species over aluminum nitride species. Continued deposition of aluminum produces aluminum layers over the initial oxide layer. The DSC data demonstrates an increase in decomposition energy through the placement of metal directly onto the explosive surface.

11:00am **SS1+AS+TF-ThM10 Characteristics and Stability of Oxide Films on Plutonium Surfaces**, ***H.G. García Flores***, University of Nebraska-Lincoln and Los Alamos National Laboratory, *A.L. Broach, D.P. Moore*, Los Alamos National Laboratory, *D.L. Pugmire*, Los Alamos National Laboratory and University of Nebraska-Lincoln

The oxidation of plutonium metal continues to be an area of considerable activity. The reaction characteristics have significant implications for production use, storage, and disposition of this reactive material. Developing an accurate physical model of the structures, oxidation states, and oxygen concentration gradients present during oxidation are essential to understanding this process. Traditionally, the stable oxides of plutonium have been thought to be plutonium sesquioxide (Pu_2O_3, O/Pu=1.5, Pu^{3+}) and plutonium dioxide (PuO_2, O/Pu=2.0, Pu^{4+}), existing in a layered structure on oxidized plutonium metal. Many studies of this system are performed under ultra-high vacuum (UHV) using surface sensitive techniques to probe oxidation states, electronic structure, and surface chemistry.

Here, we report on a detailed study using x-ray photoelectron spectroscopy (XPS) and Auger electron spectroscopy (AES) to measure the relative concentrations of oxygen and plutonium, as well as the resulting oxidation states in the near-surface region. It has previously been shown that under UHV conditions, PuO_2 undergoes an auto-reduction reaction to the more stable Pu_2O_3. The auto-reduction of PuO_2 occurs as oxygen diffuses from the surface, through the oxide-film, to the metal-oxide interface.[1] The results of this study show a much greater than anticipated extent of auto-reduction and challenge the commonly held notion of the stoichiometric stability of Pu_2O_3 thin-films, especially in the presence of plutonium metal. The data indicates that a hypo-stoichiometric plutonium oxide (Pu_2O_{3-y}) exists at the metal-oxide interface. A new model of the plutonium/oxygen thin-film system will be proposed and its applicability to thicker-films will be discussed.

---

[1] Morrall P, Tull S, Glascott J, Roussel P, 2007 *J.Alloys Comp.* **444-445** 352.

Surface Science
Room: N - Session SS2-ThM

Electron Activated Molecular Interfaces
Moderator: S.L. Tait, Indiana University

8:00am **SS2-ThM1 Thermal Effects of Templated C_{60} Ordered Structures on AnCA**, ***B. Xu***, Yanshan University, China

Anthracene carboxylic acid (AnCA) forms multiphase self-assembly structures on Ag(111). Two of these multiphase structures were employed to investigate the template effects on sequentially deposited C_{60} molecules using scanning tunneling microscopy. At low C_{60} coverage, fullerene molecules tend to occupy Ag step edge or AnCA domain boundary sites. With increasing C_{60} deposition, strong modulation on C_{60} growth was observed depending on the initially AnCA structures. C_{60} can either pair into dimers and locate on top of AnCA molecules with the periodicity determined by the underneath AnCA (Interface I), or form small phase-separated C_{60} and AnCA domains with the width of tens of nanometers (Interface II). Anneal these interfaces at 370 K lead to the desorption of most of the AnCA molecules and the formation of novel C_{60} structures. For Interface I, the second layer C_{60} molecules are organized into ordered dimers on top of the first layer zigzag C_{60} chains running along Ag[1-10] direction. The distance between neighboring zigzag C_{60} chains is 2 nm, and there are some AnCA molecules left between the zigzag chains to hold the structure stable. For Interface II, parallel C_{60} chains along Ag[11-2] are observed after annealing. The C_{60} molecules are close packed along the chain direction and separated by *c.a.* 1.3 nm between neighboring chains. The molecules have alternative heights across the chain direction, suggesting distinct molecular orientations. Our studies suggest a pathway of nanostructure fabrication through the choice of suitable template and annealing treatment.

8:20am **SS2-ThM2 Porphyrin Adsorption on Copper Single Crystal Electrodes Studied by SXPS**, ***S. Breuer***, *D.-T. Pham*, University of Bonn, Germany, *G. Cherkashinin, T. Meyer*, Technical University of Darmstadt, Germany, *P. Broekmann*, University of Berne, Switzerland, *K. Wandelt*, University of Bonn, Germany

Porphyrins are well known as biologically active molecules, e.g. as heme in hemoglobin or chlorophyll in green leaves. Their biological functions originate from their redox activity, which makes their investigation in an electrochemical environment interesting. We have investigated the electrochemically deposited monolayers of Tetra-methylpyridinium-porphyrin (TMPyP)-Tetratosylat on chloride and sulphate precovered Cu(100) and Cu(111) surfaces by means of Cyclic Voltametry (CV), in-situ ElectroChemical Scanning Tunneling Microscopy (EC-STM) as well as ex-situ X-ray Photoelectron Spectroscopy with synchrotron radiation S-XPS at the SoLiAS-station at BESSY II. This station allows the electrochemical preparation of the surfaces and a quick and contaminationfree transfer into UHV. The electrochemical preparation includes the formation of the anion preadsorption in diluted hydochloric- or sulphuric-acid, respectively, and the adsorption and emersion of the porphyrin layer at different potentials within the doublelayer regime.

While the preadsorbed anion layers, i.e. c(2x2) Cl^- on Cu(100), $(\sqrt{3}x\sqrt{3})R30°$-Cl^- on Cu(111), quasi- $(\sqrt{3}x\sqrt{7})R30°$-SO_4^{2-} on Cu(111) and a disordered SO_4^{2}-layer on Cu(100), bind the TMPyP-cations electrostatically to the surface variation of the electrode potential causes structural transitions within the selfassembled porphyrin layers, as seen with EC-STM. The S-XPS N(1s) spectra enable a clear correlation of the structural changes with concommitant redox-transition of the TMPyP-cations. As a result structural transitions within the ordered TMPyP-layers are most likely due to different lateral electrostatic interactions between different TMPyP-redox states.

8:40am **SS2-ThM3 STM and XPS Study on the Reactive versus Non-Reactive Adsorption of Viologens**, *D.-T. Pham, C. Safarowsky, S. Huemann, S. Breuer*, University of Bonn, Germany, *R. Hunger*, Technical University of Darmstadt, Germany, *P. Broekmann*, University of Berne, Switzerland, ***K. Wandelt***, University of Bonn, Germany

The reactive and non-reactive adsorption of redox-active viologens (1,1`-disubstituted-4,4`-bipyridinium molecules) on a chloride modified copper electrode has been studied using a combination of cyclic voltammetry (CV), in-situ scanning tunneling microscopy (STM) and ex-situ photoemission techniques. Two prototypes of viologens, 1,1`-dibenzyl-4,4`-bipyridinium molecules and 1,1`-diphenyl-4,4`-bipyridinium molecules (abbreviated as DBV and DPV respectively), are studied here with respect to their redox behaviour upon adsorption on a chloride modified copper surface. DBV molecules can be adsorbed and stabilized on a chloride modified Cu(100) electrode surface in their di-cationic state at potentials above the main reduction wave in the cyclic voltammogram. Electrostatic attraction between the solvated viologen di-cations and the anionic chloride layer is the main driving force for the DBV adsorption onto the electrode surface. By reducing the adsorbed dicationic DBV^{2+} species to the corresponding radical mono-cation $DBV^{\bullet+}$, a quasi-reversible phase transition is initiated from a "cavitand" to a "stripe pattern" phase on the chloride layer. Analysis of the N1s and O1s core level shifts of the adsorbed DBV molecules points to a *non-reactive* DBV adsorption leaving the DBV^{2+}_{ads} solvation shell partly intact. The laterally ordered DBV^{2+}_{ads} monolayer is highly hydrophilic with at least 8 water molecules per viologen present within this cationic organic film. The analysis of the Cl2p core level shift reveals that no other chloride species is present on the surface than the one underneath the organic molecules in direct contact with the metallic copper surface.

DPV^{2+} molecules are much more reactive upon adsorption and cannot be stabilized on the electrode surface in di-cationic state, at least within the narrow potential window of copper. The N1s core level shift points to DPV^{2+} molecules which are upon adsorption instantaneously reduced to the corresponding mono-reduced $DBV^{\cdot+}_{ads}$ species even at potentials above the main redox wave in the voltammogram. This process leads to the formation of a highly hydrophobic monolayer film with polymeric $DBV^{\cdot+}_{ads}$ stacking chains as the characteristic structural motif .

9:00am **SS2-ThM4 Interfacing Electrocatalytic Molecules with Vertically Aligned Carbon Nanofibers through Click Chemistry: An Approach to "Smart", Highly Functional Nanostructures**, ***E.C. Landis***, *R.J. Hamers*, University of Wisconsin, Madison

Vertically Aligned Carbon Nanofibers are a unique form of nanoscale carbon comprised of graphene cups nested together to form a nanofiber. A unique feature of VACNFs is that they expose large amounts of graphene edge-planes along the nanofiber sidewalls. The high electron transfer rates associated with edge plane graphite suggest that VACNFs should be an excellent support for electrocatalysis. However, nanofibers alone lack the specificity often desired in electrochemical reactions. We have developed a method for covalently binding redox active molecules to the VACNF surface based on "click" chemistry as a pathway toward combining the high stability of VACNFs with the selectivity provided by molecular redox-active groups. This binding method creates a highly stable linkage of VACNFs to a 'smart' ligand with well defined redox properties. Using XPS, FTIR, and other surface analytical methods in conjunction with electrochemical measurements, we have investigated how the nanoscale structure of the fibers and the nature of the surface ligands impacts the surface chemistry and subsequent electron transfer processes. Our results demonstrate that the graphitic edge-plane sites of VACNFs play a key role in the chemical reactivity of VANCFs and in the subsequent electron-transfer processes on VACNFs functionalized with redox-active groups. These results demonstrate that VACNFs are a promising material for functional nanostructures using covalently tethered molecular catalysts.

9:20am **SS2-ThM5 Fabrication of a Full-Coverage Polymer Nanobrush on Electron-Beam-Activated Monomolecular Template**, ***S. Schilp***, *N. Ballav, M. Zharnikov*, University of Heidelberg, Germany

Along with chemistry, morphology is an important tool to adjust properties of surfaces and interfaces. One of the most promising approaches to control over surface morphology down to the nanometer scale is the fabrication of 3D polymer brush patterns by surface-initiated polymerization (SIP) combined with electron beam lithography (EBL). However, polymer brush patterns made by EBL-SIP are chemically inhomogeneous. Whereas the polymer brush itself is comprised of a polymer, the areas between the 3D features have a different chemical identity determined by the original template. As a result, the effects of morphology on one side and chemistry and surface energy on the other side can be entangled when using such patterns as model surfaces for, e.g., biology-inspired research. Here, we show that this drawback can be overcome by using a sophisticated primary template comprised of monomolecular film with mostly deactivated amino tail groups suitable for SIP. Whereas SIP on such a template gives a thin, homogeneous "background" brush, the regeneration of these groups by electron beam activation lithography promotes the controlled growth of 3D polymer features on this background, resulting in the formation of chemically homogeneous morphology pattern exclusively comprised of the polymer material. The technique relies upon commercially available compounds and requires a comparably low patterning dose. Using a biologically relevant polymer, poly-N-isopropylacrylamide, as a test system, we demonstrated the fabrication of both complex gradient-like brushes and marine-mammals-skin-inspired surfaces on the electron-beam-engineered monomolecular templates.

9:40am **SS2-ThM6 Self-assembled Monolayers as Templates for Electrochemical Nanotechnology**, ***C. Shen***, University of St Andrews, UK, *C. Silien,* University of Limerick, Ireland, *M. Buck*, University of St Andrews, UK

Electrochemistry and self-assembled monolayers (SAMs) are a versatile combination as, on the one hand, SAMs can be used as templates to control electrochemical processes whereas electrochemistry, on the other hand, allows manipulation of SAMs [1,2].

Within this context underpotential deposition (UPD) of metal, i.e. intercalation of a metal monolayer at the SAM-substrate interface, is particularly interesting as this alters the electrochemical stability of a SAM. However, to exploit this for a controlled manipulation of SAMs on the nanoscale it is mandatory to use SAMs of very high quality in order to eliminate uncontrolled metal UPD caused by defects in a SAM [3]. In our experiments we use a class of thiol SAM whose molecules are characterized by the combination of a rigid aromatic moiety with an aliphatic spacer. Forming layers of high structural perfection defects are then introduced in a controlled way by

local modification of a SAM using, for example, the tip of a scanning tunneling microscope. By this means UPD of metal and subsequent modification of the SAM can be controlled on a length scale ranging from micrometers down to nanometers.

[1] Thom, I. ; Hähner, G.; Buck, M. Appl. Phys. Lett. 87, 024101 (2005).

[2] Oyamatsu, D.; Nishizawa, M.; Kuwabata, S.; Yoneyama,

H. Langmuir 14, 3298 (1998).

[3] Silien, C.; Buck, M. J. Phys. Chem. C 112, 3881 (2008).

10:40am **SS2-ThM9 XPS and AFM Characterization of Two Component Self-Assembled Monolayers on Au(111)**, ***M.H. Cheng***, *T. McIntire, R.L. Grimm, J.C. Hemminger*, University of California, Irvine

Water uptake on organic films is of great importance in a number of fields. We have used two-component alkanethiol self-assembled monolayers (SAMs) to prepare surfaces with varied hydrophilic character. These surfaces have been used to study water uptake as a function of hydrophilic/ hydrophobic character. The chemical composition and morphology of the two two-component alkanethiol self-assembled monolayers on Au(111) were characterized by x-ray photoelectron spectroscopy (XPS) and atomic force microscopy (AFM). Gold films on glass were prepared by piranha cleaning and *in vacuo* argon ion sputtering yielding carbon- and oxygen-free surfaces. Solution-phase chemistry forms a two-component SAM comprised of the octanethiol and 6-mercaptohexanoic acid. These components were selected for comparison with previous research in our laboratory regarding the interaction and temperature-programmed desorption (TPD) of water from organic surfaces of tuned hydrophobic and hydrophilic character. The ratio of the O(1s) to the Au(4f) peak areas in the XPS quantify the relative fraction of the carboxylic acid-terminated thiol in the SAM. The XPS spectra indicate that the relative fraction of the two thiol components in the surface adsorbed SAM phase does not correspond to the relative solution-phase concentrations. By comparison with water thermal desorption experiments, we discuss the implications for the interaction of water with methyl-terminated and carboxylic acid-terminated organic surfaces and partially-oxidized organic aerosol.

11:00am **SS2-ThM10 Vacancy Diffusion in Self-Assembled Organic Monolayers and its Role as a Roughening Mechanism in Organic/Organic Interfaces**, ***C. Urban***, *D. Ecija, M. Trelka,* Universidad Autonoma de Madrid, Spain, *R. Otero,* UAM & IMDEA-Nano, Spain, *J.M. Gallego,* ICMM-CSIC, Spain, *N. Martín,* Universidad Complutense de Madrid, Spain, *R. Miranda*, UAM & IMDEA-Nano, Spain

Molecular diffusion on solid surfaces is of fundamental importance for surface chemistry and also because of the important role it plays in the formation of self-assembled molecular mono and multilayers. Many studies have discussed the diffusion processes of a single, isolated molecule on the surface and the self-assembly process in terms of molecule-molecule and molecule-susbstrate interactions, but the relevant kinetic aspects have mostly not been dealt with. In addition, the growth of organic multilayers of two different types of functional molecules (e.g. donor and acceptor or magnetic and non-magnetic) with enough structural perfection requires a knowledge of intermixing processes at interfaces not yet available and intimately related to vacancy diffusion.

We directly visualized the surface diffusion of molecular vacancies in monolayers of exTTF (2-[9-(1,3-dithiol-

2-ylidene)anthracen-10(9H)-ylidene]-1,3-dithiole) self-assembled on Au(111) under UHV conditions. exTTF is a strong electron donor, and in combination with PCBM, it has been shown to produce a phase-segregated, mixed layer with optimal morphology for bulk heterojunction solar cells [1]. When deposited on Au(111), exTTF molecules modify the substrate surface reconstruction and self-assemble to form long rectangular islands, the space between them being occupied by a sea of diffusing, non-nucleated molecules, which are very mobile even down to 150 K. The continuous exchange of molecules between the islands and this sea creates many vacancies within the islands. By means of a variable temperature fast-STM, we have quantified the diffusion of these vacancies within the islands. The results indicate a non-isotropic, Brownian-type diffusion. The implication of these results and the relevance of this diffusion mechanism for the exchange processes observed in the growth of exTTF-PCBM mixed layers and multilayers will be discussed.

[1] R. Otero, D. Écija, G. Fernández, J.M. Gallego, L. Sánchez, N. Martín, R. Miranda, Nano Letters 7 (2007) 2602-2607.

11:20am **SS2-ThM11 Local Fluctuations in Organic Adlayers - a Quantitative Video-STM Study**, ***M. Roos***, *T. Waldmann, H.E. Hoster, R.J. Behm*, Ulm University, Germany

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen-bonded networks on different substrates at solid surfaces.[1,2] Using time resolved scanning tunneling microscopy we have studied selected dynamic phenomena in such adlayers on Au(111) and Ag(111) at around room temperature. Specifically, we have evaluated the mobility of defects in ordered adlayers, exchange of molecules between 2D phases of different local coverage and structure and fluctuations within disordered phases. Such data not only provide important information about typical rates in self assembly processes, but also give quantitative insights into molecular-scale aspects that govern the adlayer thermodynamics. Apart from the balance of molecule-molecule and molecule-substrate interactions, we find a surprisingly high influence of molecular entropy due to rotation and translation on the stability of the distinct phases. We will discuss the relevance of our findings for these particular model systems for the growth and stability of supramolecular structures in general.

[1] M. Roos et al., Phys. Chem. Chem. Phys. 9 (2007) 5672.

[2] H. E. Hoster et al., Langmuir 23 (2007) 11570.

11:40am **SS2-ThM12 From Self-Assembled Monolayers to 1 nm Thin Conducting Carbon Nanosheets**, ***A. Turchanin***, *A. Beyer, Ch.T. Nottbohm, X. Zhang,* University of Bielefeld, Germany, *R. Stosch,* PTB-Braunschweig, Germany, *A. Sologubenko, J. Mayer,* University of Aachen, Germany, *P. Hinze, T. Weimann,* PTB-Braunschweig, Germany, *A. Gölzhäuser*, University of Bielefeld, Germany

Whereas the fabrication of free-standing 0D and 1D nanomaterials like clusters, nanoparticles, nanowires, nanotubes etc. is well established at present, the fabrication of free-standing 2D materials with atomic thicknesses is not routine. In this contribution we present a route for the fabrication of novel ultrathin (~1 nm) free-standing carbon nanosheets with adjustable sizes based on molecular self-assembly. Self-assembled monolayers (SAM) of aromatic biphenyl molecules are first cross-linked by electrons [1]. Vacuum pyrolysis of the cross-linked films transforms them into a mechanically stable and conductive 2D graphitic phase consisting of nanosize graphene patches [2, 3]. Resistivity and stiffness can be tuned by the annealing temperature [3]. The transition from insulator to conductor (~100 kΩ/sq) is characterized by a variety of complementary spectroscopic and microscopic techniques (Raman Spectroscopy, XPS, UPS, NEXAFS, TDS, HTEM, STM, AFM). A plethora of applications of this novel material is visible taking advantage of the fact that size, shape, and resistivity of the nanosheets in supported and suspended states (nanomembranes) are easily controlled.

[1] W. Geyer, V. Stadler, W. Eck, M. Zharnikov, A. Gölzhäuser, M. Grunze, *Appl. Phys. Lett.* **75**, 2401 (1999)

[2] A. Turchanin, M. El-Desawy, A. Gölzhäuser, *Appl. Phys. Lett.*, **90**, 053102 (2007)

[3] A. Turchanin, A. Beyer, Ch. T. Nottbohm, X. Zhang, R. Stosch, A. Sologubenko, J. Mayer, P. Hinze, T. Weimann, A. Gölzhäuser, *Adv. Mater.* **21,** 1233 (2009)

Thin Film
Room: B4 - Session TF-ThM

Nanostructuring Thin Films II
Moderator: P.D. Rack, University of Tennessee

8:00am **TF-ThM1 Nanostructure of Gold Film Over Vertically Aligned Carbon Nanofiber Surface Impact on Immobilization of Alkanethiols**, ***R. Desikan***, North Carolina State University, *T.E. McKnight,* Oak Ridge National Laboratory, *P.D. Rack,* University of Tennessee, *A.V. Melechko*, North Carolina State University

Chemical self-assembly has been widely used for several applications including surface modification and functionalization. The physics and chemistry of alkanethiol self-assembled monolayers (SAM) has been extensively studied. It is well known that SAM structures of alkanethiol are strongly influenced both by the surface structure of the underlying gold substrate. It has also been shown that the adsorption of alkanethiols onto gold surfaces having large, flat grains produces high-quality self-assembled monolayer. In this study we have investigated the effect of SAM formation over carbon nanofibers coated with gold thin film. The film nanostructure is strongly affected by the morphology of the surface on these high aspect ratio 3D features. The thiolated molecules are chosen due to the strong affinity of sulfur head groups with the gold surface of the carbon nanofibers. The difference in surface stress response alkanethiol of adsorption in vapor phase on large- and small-grained gold correlates well with differences in alkanethiol coverage and SAM structure on those substrates. We will present observations of how the surface structure of the underlying gold substrate influences the kinetics of SAM formation. It has been shown earlier that in the case of gold surfaces with small grain sizes (<100 nm), access to the high coverage, standing-up phase is inhibited. A comparison of annealed for increasing grained gold surfaces on the fibers to as deposited film will be discussed. The characterization of molecular coverage as a function of the gold grain size with an x-ray photoelectron spectroscopy will be presented.

8:40am **TF-ThM3 Spontaneous Growth of In-whiskers from In-Y Thin Films Prepared by Combinatorial Magnetron Sputtering Technique**, ***T. Takahashi***, *A. Abdulkadhim, D. Music, J.M. Schneider*, RWTH Aachen University, Germany

In-Y binary thin films with a composition gradient were prepared using a combinatorial magnetron sputtering technique. In-whiskers grow spontaneously from the film surface at room temperature upon exposure to air. Whisker morphology and population vary with the In to Y ratio. An appreciable amount of In-whiskers is formed at film compositions close to In-25 at.%Y. The In-whisker thickness ranges from a few hundreds nanometers to a few micrometers.

In order to identify the whisker growth mechanism, temporal changes of the film surface upon air exposure were captured using scanning electron microscopy. X-ray micro diffraction was employed for studying the structural evolution during the In-whisker growth in air. The results show that the In-whiskers grow not from the tip but from the root. The whisker growth rate was as high as 150 nm/s. The growth of In-whiskers is found to be related to the incorporation of oxygen into the film during air exposure. Correspondingly, the In concentration within the film decreases as In-whiskers grow. The mechanism of the spontaneous In-whisker growth presented here can be understood based on the stress-induced extrusion of In-whiskers due to the selective room temperature oxidation of Y in sputtered In-Y thin films.

9:00am **TF-ThM4 Photothermally Induced Microchemical Functionalization of Organic Monolayers**, ***A. Schroeter***, *B. Klingebiel, N.O. Hartmann*, University of Duisburg-Essen, Germany

Photochemical routines are widely recognized as a versatile means to fabricate multifunctional patterned organic monolayers with laterally alternating chemical terminations. The lateral resolution, in turn, usually is limited by optical diffraction, that is, the fabricated structures are not much smaller than the wavelength even when highly focusing optics are used. A simple routine for sub-wavelength nanopatterning of organic monolayers relies on photothermal processes, which take advantage of nonlinear effects [1]. In photothermal processing a focused laser beam is used to locally heat the substrate and initiate thermal decomposition of the monolayer. Silane-based monolayers can be patterned from the micrometer-range down to the sub 100 nm range. In analogy to photochemical routines, it is tempting to explore photothermal procedures which allow to locally functionalize organic monolayers. Here we report on a simple photothermal procedure for local bromination of organic monolayers [2]. Surface-oxidized silicon samples are coated with alkylsiloxane monolayers. Local irradiation with a focused beam of an argon ion laser ($\lambda = 514$ nm) in gaseous bromine leads to bromination of the monolayer in a confined micrometer-sized reaction zone. While irradiation induces photolysis of bromine molecules in the gas phase, the local temperature rise of the substrate in the focal area allows for bromination of the alkyl chains. Thus locally brominated surface structures are fabricated. In conjunction with other chemical transformations this provides an efficient route to a broad variety of functional groups. This allows to build up functional surface architectures via directed self-assembly of nanoscopic building blocks such as noble metal nanoparticles and stimuli-responsive polymers. Mechanistic aspects and prospects of photothermal routines in micro- and nanofabrication of multifunctional organic monolayers are discussed.

1. D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, Nano Lett. 6 (2006) 2358.

2. B. Klingebiel, A. Schröter, S. Franzka, N. Hartmann, ChemPhysChem, in press.

9:20am **TF-ThM5 Composite Nanoparticles Produced Using Plasma-Enhanced Chemical Vapor Deposition of SiO_2 and Amine-Containing Films**, ***J.C. Shearer***, *E.R. Fisher*, Colorado State University

TiO_2 and Fe_2O_3 nanoparticles are of significant importance in both chemical and biological applications. TiO_2 nanoparticles are used in paint, coatings, food, solar technology and many other areas. Fe_2O_3, as well as other magnetic nanoparticles, are used in the biomedical industry in drug delivery schemes as well as for magnetic resonance imaging contrast agents. Silica-coated TiO_2 and Fe_2O_3 nanoparticles have distinct properties and enhanced functionality over those of uncoated nanoparticles. Plasma-enhanced chemical vapor deposition (PECVD) was employed to conformally coat TiO_2 and Fe_2O_3 nanoparticles with SiO_x and amine-containing films, thereby creating composite nanomaterials. Hexamethyldisiloxane (HMDSO)/O_2 plasmas were used to create SiO_2 and $SiO_xC_yH_z$–coated nanoparticles and pulsed hexylamine (HexAm) plasmas were used to create amine-containing hydrocarbon materials, all of which were analyzed using Fourier-transform infrared spectroscopy (FTIR), x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), and magnetic susceptibility. Films deposited on the nanomaterials showed little difference from those deposited on flat substrates. The performance of the TiO_2 nanoparticles was tested using UV-vis spectroscopy to determine dispersion characteristics of SiO_x-coated TiO_2 materials, which can give information about the agglomeration of the nanoparticles in solution. Notably, the coated materials stay dispersed longer in polar solvents, suggesting the coated nanoparticles may be better suited for applications involving colloidal suspensions. Magnetic susceptibility characterized the magnetic properties of the Fe_2O_3 nanoparticles before and after film deposition. Comparison of the mechanical and chemical properties of different composite nanomaterials will be discussed along with the influence of film composition on performance.

9:40am **TF-ThM6 Tailoring Local Conductivity by the Formation of Ag Nanoparticles in SiO_2 Xerogel Films**, ***M.F. Bertino***, *R.J. Caperton, A.A. Baski*, Virginia Commonwealth University

Thin SiO_2 xerogel films (~200 nm) were fabricated by dip coating and were doped with Ag^+ by adding $AgNO_3$ to the parent solution. Nanoparticles were then fabricated inside the pores of these films by either exposing them to ultraviolet (UV) illumination or by locally injecting charge using a conducting atomic force microscope (CAFM). In both cases, reduction of the Ag^+ ions to the metallic state and the subsequent formation of Ag nanoparticles was observed by optical absorption spectroscopy and X-ray diffraction. Surprisingly, the formation of these Ag nanoparticles was accompanied by a decrease in the electrical conductivity of the films. For exposed regions with nanoparticle formation, CAFM measurements demonstrated no measurable current (< 1 pA) at sample bias voltages above 10 V. We attribute this decreased conductivity to a change in the morphology of the conducting Ag species in the film. Before reduction, Ag^+ ions are attached to negatively charged pore walls in a comparatively dense packing and produce a conducting film. After reduction with UV exposure or CAFM charge injection, the silver metal agglomerates into conducting nanoparticles that no longer form a percolated network, leading to insulating behavior. Local modification of the conductivity on the nanometer-scale is possible by operating the CAFM with an applied voltage above 6 V and scanning a defined pattern. Subsequent imaging of the area at lower voltage then shows insulating behavior in the previously patterned regions. Larger-scale patterning on the micron-to-mm scale is possible by utilizing a mask when exposing the film to UV illumination. Extensions of this method to the fabrication of photonic and plasmonic devices is being explored.

10:40am **TF-ThM9 Synergistic Ag (111) and Cu (111) Texture Evolution in Phase Segregated $Cu_{1-x}Ag_x$ Magnetron Sputtered Composite Thin Films**, ***D.I. Filoti***, *A.R. Bedell, J.M.E. Harper*, University of New Hampshire

We investigated the texture and microstructure evolution of $Cu_{1-x}Ag_x$ composite thin films through x-ray diffraction pole figures as a function of composition for $x \leq 0.5$. As-codeposited at room temperature by magnetron sputtering, the fcc composite $Cu_{1-x}Ag_x$ emerge as a phase-segregated thin film, when the Ag volume fraction represents more than 15 at. % up to 50 at. %, or as a single phase thin film when Ag volume fraction represents less than 15 at. %. The texture evolution of Cu (111) and Ag (111) in phase-segregated Cu-Ag thin films proves to be synergistically enhanced when compared to pure copper or silver thin films. Not only is a stronger perpendicular (111) fiber texture obtained, but also an in-plane alignment of Ag (200) develops related to deposition direction and composition. By the use of transmission electron microscopy we observed a decrease in grain size in Cu-Ag composite films as compared with pure copper and silver films. These Cu-Ag thin films are being evaluated for antimicrobial applications.

11:00am **TF-ThM10 Plasmonic Phenomena in Indium Tin Oxide and ITO-Au Hybrid Films**, *S. Franzen, C. Rhodes, M. Cerruti, R.W. Gerber,* ***M. Losego***, *J.-P. Maria, D.E. Aspnes*, North Carolina State University

For more than 100 years the plasmonic periodic table has been dominated by two elements, Ag and Au. The change in the surface plasmon polariton (SPP) signal in Au thin films is currently one of the most widely used methods for detecting binding interactions in biological systems. Despite broad interest, there has been sparing fundamental research into new plasmonic materials. Here, we elucidate some equivalences regarding plasmonic phenomena in conducting metal oxides, specifically indium tin oxide (ITO), and Au. In contrast to Ag and Au, conducting metal oxides offer the possibility of tuning both the location of the metallic resonance and its width according to deposition conditions. We investigate properties of ITO and ITO/Au layers by reflectance spectra R_p and R_s obtained for light polarized parallel and perpendicular, respectively, to the plane of incidence. Data were obtained in the Kretschman configuration. These data reveal two distinct types of plasmonic phenomena, one due to a capacitive-type oscillation that can only occur for very thin conducting films and the second being the usual surface plasmon resonance. One or the other can be realized either by changing the ITO thickness or by depositing either metallic or nanostructured Au on the ITO to change boundary conditions. The results can be understood completely through a combination of the Drude model for free carriers in a metal, Bruggeman effective-medium theory, and the Fresnel equations. This provides a new dimension for engineering plasmonic phenomena for investigations of molecules adsorbed at interfaces.

11:20am **TF-ThM11 Micro and Nanostructured Interfaces for Therapeutic Delivery**, ***T.A. Desai***, University of California, San Francisco **INVITED**

Efficient drug delivery remains an important challenge in medicine. Continuous release of therapeutic agents over extended time periods and in accordance to a pre-determined temporal profile; local delivery at a constant rate to overcome systemic toxicity; improved ease of administration, and increasing patient compliance are some of the unmet needs of the present drug delivery technology. This talk will discuss in vivo drug delivery strategies that capitalize on the strengths of micro and nanofabrication. By taking advantage of our ability to control topography and chemistry at submicron size scales, we have developed organic and inorganic interfaces which modulate cell function while at the same time allow for controlled drug release kinetics. Due to our ability to create monodisperse features (pores, wires, and hollow tubes)as small as several nanometers in a variety of non-planar biocompatible materials, these interfaces offer advantages in their reproducibility, stability, and their ability to intimately contact cell and tissue surfaces. Such nanoengineered interfaces may be optimized for biomolecular selectivity and surface bioactivity, leading to unique interfacial properties not achieved through existing drug delivery approaches. Nanotechnology can add functionality to current drug delivery platforms while becoming an enabling technology leading to new basic discoveries in the biological sciences.

Applied Surface Science
Room: C2 - Session AS-ThA

Chemical State Depth Profiling
Moderator: G.L. Fisher, Physical Electronics

2:00pm **AS-ThA1 Factors Affecting XPS Sputter Depth Profiling of Organic Materials**, ***S.J. Hutton***, *I.W. Drummond, S.C. Page, C.J. Blomfield*, Kratos Analytical Ltd, UK

The sputter profiling of *inorganic* materials during X-ray Photoelectron Spectroscopy (XPS) is a well established technique to investigate quantitative chemical composition variations with depth. Until recently XPS sputter depth profiling of *organic* materials has suffered from several seemingly intractable problems, not least the significant ion induced surface damage. Secondary Ion Mass Spectroscopy (SIMS) of organic materials using noble gas or liquid metal ion sources suffered related problems. These problems have largely been overcome for the SIMS analysis of a wide range of organic materials by the introduction of cluster ion sources such as SF_5 and C_{60}. Advantages of cluster sources include an increase in secondary ion yield over conventional mono-atomic sources and a reduction in beam induced damage of the surface.

Following on from these innovations in SIMS, cluster ion sources have been utilised for XPS sputter profiling of organics. These sources have been shown to significantly reduce ion induced surface damage of organic materials as measured by XPS thus making the XPS sputter profiling of organic materials feasible.

In this study we investigate the sputter profiling of several model polymer films using a new polyaromatic hydrocarbon (PAH) (coronene) cluster ion source. Initial results demonstrate that yield volumes per incident ion are dependent on the nature of the polymer, with approximate values of: 90 nm^3 for poly(lactic-co-glycolic acid) (PLGA); 117 nm^3 for polyacrylic acid (PAA); and 142 nm^3 for polylactic acid (PLA). Other polymers, such as polystyrene (PS), do not appear to be sputtered by cluster sources under the currently reported conditions. Early results also indicate that various experimental parameters, such as incident beam energy, affect the sputter yield and amount of ion beam induced surface damage.

Clearly there is a need to investigate the various parameters which may influence ion yields and damage with the aim of optimising sputtering conditions for a range of organic materials. The work presented here attempts to elucidate the effects of variables such as ion incident energy; ion beam angle of incidence; sample temperature and ion mass on the sputtering performance of the aforementioned PAH ion source on several thin polymer films.

2:20pm **AS-ThA2 On the Understanding and Optimization of Etching Parameters for Optimal ToF-SIMS 2D and 3D Analysis of Biological Cells**, ***J. Brison***, *D.S.W. Benoit, M. Dubey, M. Robinson, P.S. Stayton, D.G. Castner*, University of Washington

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) combined with cluster ion beams is now widely used to image biological samples in two and three dimensions. Cluster ion beams (e.g., Bi_3^+, C_{60}^+) have indeed been shown to provide higher molecular ion yields with lower chemical damage in depth, allowing successful 2D imaging as well as molecular depth profiling of complex biological samples. In parallel, much research has been conducted to improve the sample preparation protocols to insure that the biological samples are preserved as close as possible to the living state for ToF-SIMS analysis under ultra high vacuum (UHV) conditions.

However, ToF-SIMS is not yet routinely used to solve biological problems because the data interpretation is complicated and the fundamental cluster ion/sample interaction is not fully understood. In this work, we combined ToF-SIMS with other complementary surface characterization techniques (i.e., XPS, AFM, SEM, etc.) to supplement the complex ToF-SIMS 2D and 3D datasets obtained from biological samples. For this purpose, human HeLa cells were seeded on silicon substrates and prepared according to different protocols (fixation with paraformaldehyde, cryofixation, etc.) for UHV analysis. The HeLa cells were also treated with bromine labeled small interfering RNA (siRNA) and with bromodeoxyuridine (BrdU) to provide a target for ToF-SIMS and XPS analysis. A series of ToF-SIMS experiments dealing with the different ion species (Bi_1^+, Bi_3^+, and C_{60}^+), and various beam parameters (single beam, dual beam, different energies and fluences) was designed to obtain a reproducible and reliable depth profile of single HeLa cells when analyzed by the above listed techniques. XPS along with principal component analysis, for the first time has been used to image and provide quantitative elemental information about individual cells. Our results also show that AFM and SEM provide a better understanding of the effect of topography on the ToF-SIMS data.

2:40pm **AS-ThA3 On the Way to Optimal 3D Molecular Imaging with ToF-SIMS: A Comparison between C_{60} Single Beam and Bi_n/C_{60} Dual Beam Depth Profiling**, *J. Brison*, ***S. Muramoto***, *D.G. Castner*, University of Washington

Many ToF-SIMS 3D molecular images are acquired in the dual beam mode, where a high-energy beam (e.g., Ga+ or Bin+ at 25keV) used at low fluence for analysis is combined with a low-energy beam for sputtering/etching (e.g., C60n+ at 10 keV, Cs+ at 250 eV). Because its fluence is kept below the static limit, the effect of the high-energy analysis beam is sometimes neglected in the data interpretation, with the chemical damage entirely attributed to the etching beam. The influence of the analysis beam on the quality of ToF-SIMS depth profiles has been studied for inorganic samples [1], but no systematic study has been reported for organic samples. Because organic samples, and specifically biological samples and cells, are complex and fragile, a systematic study is necessary to understand, quantify, and model the influence of the ToF-SIMS parameters on the quality of ToF-SIMS 3D molecular images. These parameters include the species, fluence, energy, bombardment angle, and electrical charge of each primary ion beam.

In this paper, we have performed multiple depth profiles of a polymeric sample (100 nm thick tetraglyme on Si) in the single beam mode (C60 for analysis and etching) and compared them to those obtained in the dual beam mode (Bin+ for analysis and C60n+ for etching). For all depth profiles we kept the same parameters for the etching beam (i.e., C60 at 10 keV, 500 x 500 μm2, 1nA) and we varied the analysis conditions (i.e., species, area, energy, and fluence). We found that the analysis beam could significantly improve or degrade the quality of ToF-SIMS depth profiles, depending on the analysis beam parameters. At very low fluence (3 to 8% of the total primary ion fluence, depending on the sample and on the ion species), Bin+ improves the quality of the ToF-SIMS 3D images because of its higher lateral resolution. At higher Bin+ fluences, the high clean up efficiency of the C60 beam [2] can no longer remove the chemical damage induced by the analysis beam and the quality of ToF-SIMS data (molecular signals and interface width) degrades with the increasing Bin+fluence (or decreasing C60 fluence).

[1] T. Grehl, R. Mollers, E. Niehuis, Appl. Surf. Sci. 203-204 (2003) 277.

[2] A. Wucher, J. Cheng, N. Winograd, J. Phys. Chem. C 112 (2008) 16550.

3:40pm **AS-ThA6 Teaching Laser Desorption Mass Spectrometry Old and New Tricks in Postionization and Depth Profiling**, ***L. Hanley***, University of Illinois at Chicago **INVITED**

Secondary ion mass spectrometry (SIMS) has seen improvements in spatial and depth resolution that now approach the tens of nanometer limit for even polymeric and biological samples. Laser desorption-based strategies such as matrix-assisted laser desorption ionization (MALDI) and laser desorption postionization mass spectrometry (LDPI-MS) [1,2] display spatial resolution that barely approaches one micron. Depth resolution in laser desorption methods is even worse at tens of microns and typically requires new sample sections to be prepared for each depth. Nevertheless, MALDI-MS and LDPI-MS remain attractive because of the more detailed chemical information they often provide, especially when applied to chemically complex samples and those with higher molecular weight species. Ultrashort pulse laser irradiation is known to cause minimal laser induced damage when interacting with soft biological materials. Data will be presented evaluating the prospects for employing ultrashort laser pulses for depth profiling in mass spectrometric imaging. Ongoing experiments utilizing single photon ionization of laser desorbed neutrals via vacuum ultraviolet radiation will also be presented for detection and selectivity that are complementary to MALDI-MS. These strategies will be applied to the analysis of molecular analytes within intact bacterial biofilms grown on biomaterials surfaces.

[1] L. Hanley and R. Zimmermann, *Anal. Chem.*, to be published June 2009.

[2] G.L. Gasper, R. Carlson, A. Akhmetov, J.F. Moore, and L. Hanley, Proteom. **8** (2008) 3816.

4:20pm **AS-ThA8 Surface Damage Evaluation of Organic Materials Irradiated with Ar Cluster Ions**, ***J. Matsuo***, *S. Ninomiya, K. Ichiki, H. Yamada, M. Hada, T. Aoki, T. Seki*, Kyoto University, Japan

Soft materials, such as organic or biological materials are of interest since last decade, because of their structural, functional and environmental flexibility. However, very few techniques are available for soft material analysis, because energetic probes destroy structure and change chemical states of soft materials during the analysis. 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 molecular depth profiling with large Ar cluster ions is possible for poly-carbonate (PC) and poly-styrene (PS), which is difficult to analyze with C_{60} ion beam. These results indicate that extreme low energy beam is necessary for molecular depth profiling. In case of large Ar cluster beam, the kinetic energy of a few eV/atom, which is comparable to the bonding energy of molecules, is realized. In addition to this, no Ar remains on the surface, because of its low binding energy. Therefore, Large Ar cluster ion beam irradiation rarely leads to damage accumulation on the surface of the polymers, and these characteristics as etching beam are also suitable for other depth profiling techniques. The surface chemical states of the polymers were measured with X-ray photoelectron spectrometry (XPS) before and after etching. The chemical states of the poly m ethyl methacry late (PMMA) sample etched with Ar atomic ion beams differed significantly from those of the unirradiated sample, whereas the chemical states were maintained even after etching with large Ar cluster ion beams. According to the detail analysis of C1s and O1s spectra, atomic composition and chemical state are very close to the ideal values.

Atomistic mechanism of energetic cluster impacts and prospect for this technique will be discussed in conjunction with possible applications.

4:40pm **AS-ThA9 Optimization of C_{60} Sputtering Conditions for Polymer Depth Profiling by TOF-SIMS**, ***S.R. Bryan***, Physical Electronics, *S. Iida*, ULVAC-PHI, Japan, *G.L. Fisher, J.S. Hammond*, Physical Electronics, *N. Sanada, M. Suzuki*, ULVAC-PHI, Japan

Depth profiling of polymer materials by Secondary Ion Mass Spectrometry (SIMS) has been practiced for many years using atomic primary ion beams such as Cs^+ or Ar^+. The analytical information provided was limited to elemental profiles due to extensive damage to the polymer structure during sputtering. The recent introduction of C_{60}^+ ion beams on TOF-SIMS instrumentation has generated significant scientific interest because of its ability to sputter a variety of organic materials to significant depths while maintaining structurally significant molecular ions in the mass spectrum. From the published studies to date, it has become clear that a high sputter yield is critical to the ability to depth profile polymers while maintaining a steady state signal of structurally significant molecular ions. In this study, we evaluate the C_{60}^+ experimental parameters of beam energy and angle of impact on the ability to depth profile several polyunsaturated polymers, such as polycarbonate (PC) and polystyrene (PS), which have proven to be difficult in earlier studies. The results verify that conditions which increase the sputter yield, such as higher beam energy or more glancing angle of impact, minimize the accumulated damage rate as a function of dose. By optimizing the C_{60}^+ sputtering conditions, the number of organic materials that can be depth profiled with acceptable damage accumulation will be significantly increased.

5:00pm **AS-ThA10 Metrics for Polymer Depth Profiling with C_{60} Ion Sources**, ***J.S. Hammond***, *S.S. Alnabulsi, S.N. Raman, J.F. Moulder*, Physical Electronics

C_{60} ion sources on XPS systems have recently been shown to provide a powerful capability for organic contamination removal and for depth profiling many organic and polymer materials. However the depth of uniform sputter yield has been found to depend on the impact energy of the C_{60} ion and the composition of the sample. To quantify the relative importance of other parameters that can extend the depth profiling range and uniformity of sputter yield during polymer depth profiling, Zalar azimuthal rotation during C_{60} sputtering, the angle of incidence of the C_{60} ion beam, sample temperature and integrated X-ray exposure has been explored. AFM imaging of the crater bottom at various depths of a sputter profiled sample has been used to characterize the sputtering process. Results will be presented for various materials using these different analysis conditions to improve the uniformity of sputter rates and interface definition of multi-layer polymer films.

5:20pm **AS-ThA11 Organic Depth Profiling of a Model Binary System: The Demonstration of Charge Transfer between Secondary Species**, ***A.G. Shard***, National Physical Laboratory, UK, *A. Rafati*, University of Nottingham, UK, *J.L.S. Lee*, National Physical Laboratory, UK, *M.R. Alexander, M.C. Davies*, University of Nottingham, UK

In recent years, it has been demonstrated that cluster ion beams may be used to ablate some materials, particularly organic materials, without the significant accumulation of damage. For such materials it is therefore possible to use cluster ion beam sputtering in conjunction with a surface analytical technique, such as SIMS or XPS, to obtain depth profiles and three-dimensional images of the distribution of species in the near-surface region. For SIMS organic depth profiling to find wide acceptance as an analytical tool it is important that it is able to measure physically meaningful quantities, such as the local concentration of a species within a blend. Building upon our recent advances in the understanding of organic depth profile using model multilayers[1], we have investigated a model miscible binary mixture of codeine and poly(lactide) using both SIMS and XPS as analytical techniques.

We show that these samples possess an overlayer of almost pure poly(lactide), which fortuitously allows the direct comparison of different samples in terms of secondary ion yield behaviour. By comparing between data obtained from samples with different concentrations, it is found that secondary ion intensities do not scale linearly with composition. However, it is possible to relate secondary ion intensities to local concentrations for a binary system. The dependence of secondary ion yield on composition is described in terms of a model based on the kinetically limited transfer of charge between secondary ions and secondary neutrals. In this case, secondary ions from codeine, which contain a basic amine group, have an enhanced yield when dilute in poly(lactide). The enhancement diminishes with increasing concentration. The suppression in secondary ion yield for ions arising from poly(lactide) has the same functional form as the enhancement for secondary ions from codeine. The model is found to describe the data very well and has some wider implications for the interpretation of SIMS data from organic systems.

[1] A.G. Shard, F.M. Green, P.J. Brewer, M.P. Seah, I.S. Gilmore, Journal of Physical Chemistry B 112 (2008) 2596-2605.

Biomaterial Interfaces
Room: K - Session BI+AS+NS-ThA

Micro and Nanoengineering of Biointerfaces I
Moderator: G.J. Leggett, University of Sheffield

2:00pm **BI+AS+NS-ThA1 Spatial Organization and the Mechanics of Signal Transduction in Cell Membranes**, ***J.T. Groves***, University of California, Berkeley **INVITED**

Signal transduction in living cells is carried out through cascades of chemical reactions, which generally begin on the cell membrane surface.

In recent years, there has been growing realization that the large-scale spatial arrangement of cell surface receptors can regulate the outcome of ensuing signal transduction process. Signaling through the T cell receptor (TCR) in the context of the immunological synapse provides a case in point. Spatial reorganization of TCRs occurs on multiple length-scales, and apparently with multiple purposes, during antigen recognition by T cells. The cell membrane and cytoskeleton, working as an inseparable unit in this case, create the mechanical framework within which TCR signaling processes occur. To better study these phenomena, a new experimental strategy, in which the spatial positions of cell membrane receptors are directly manipulated through mechanical means, has emerged. By physically inducing a 'spatial mutation' of the signaling apparatus, the role of spatial organization in signal transduction as well as the mechanisms by which it arises can be illuminated. Specific applications of this strategy to TCR signaling and other cell-cell signaling systems will be discussed.

2:40pm **BI+AS+NS-ThA3 Investigation of Array Spotting of Polymer Supported Lipid Bilayers**, ***S. Kaufmann***, *M. Homenuke*, ETH Zurich, Switzerland, *J. Sobek*, University of Zurich, Switzerland, *E.O. Reimhult, M. Textor*, ETH Zurich, Switzerland

Supported lipid bilayers (SLB) constitute a simple model of cell membranes and are of particular interest as components of future generations of biosensors based on transmembrane proteins. Techniques which are able to produce arrays with small micrometer-sized sensor areas in a cheap and fast way are beneficial. A major challenge producing such arrays of SLBs is their need for an aqueous environment during formation and operation, which has so far prevented the wide-spread use of common techniques to produce arrays such as spotting.

Poly(ethylene glycol) (PEG) can be incorporated into the membrane of liposomes through lipid molecules end-functionalized with a PEG chain and these liposomes were shown to spontaneously fuse to PEG-SLB on glass surfaces with a highly hydrated PEG cushion on each side of the membrane allowing ample space and protection for incorporation of membrane proteins[1,2]. Since Cremer and coworkers [3] also showed that with increasing PEG concentration the air-stability of PEG-SLBs increases it is a very promising SLB system to use for spotting where membrane air exposure during processing is a severe constraint.

We present an investigation of the limits to spontaneous PEG-SLB in terms of PEG-lipid density, demonstrating that crossing the mushroom-to-brush regime of polymer concentration prevents the PEG-SLB formation due to steric effects and shielding of the interactions[2]. Furthermore, we present conditions under which formation of PEG-SLBs is facilitated and can proceed by liposome fusion also in the brush regime as well as characterization of the kinetics of formation and the structure of these PEG-SLBs. The use of such buffers and liposomes for production of membrane arrays on glass using a non-contact piezo-spotter was then explored in detail in order to find optimal conditions of buffer composition and PEG concentration.

---

[1] Kaufmann, S. et al., *Soft Matter*, **2009**, accepted

[2] Diaz, A.J. et al., *Langmuir*, **2008**, 24, 6820

[3] Albertorio, F. et al., *Langmuir,* **2005***, 21*, 7476-7482

3:00pm **BI+AS+NS-ThA4 Direct Laser Patterning of Soft Matter: Photothermal Processing of Supported Phospholipid Multilayers with Nanoscale Precision**

M. Mathieu*, D. Schunk, S. Franzka, C. Mayer, E. Hasselbrink, N.O. Hartmann*, University of Duisburg-Essen, Germany

Supported phospholipid bilayers and multilayers are widely recognized as model systems of biological membranes. Recently, these coatings have also gained significant attention as flexible biomolecular matrixes in various micro- and nanofabrication schemes [1]. Here, we report on direct laser patterning of supported phospholipid bilayer stacks. Direct laser patterning techniques are widely recognized as powerful tools in rapid prototyping and small volume fabrication. They offer a high flexibility in fabrication of complex 2D structures and patterning can be carried out at fast writing speeds over macroscopic length scales at ambient pressures or even in liquids [2]. For patterning multi-layered dioleyl-phosphatidic acid (DOPA) films were deposited on native silicon samples via spin coating. Then photothermal processing with a focused laser beam at $\lambda = 514$ nm is used for removal of the coating at predefined positions without causing any significant change in adjacent areas. Moreover, processing with nanoscale precision is feasible despite the soft and fluid nature of phospholipid films. In particular, holes with diameters from 1.8 µm down to 300 nm and below are fabricated using a laser spot diameter of about 2.5 µm [3]. Furthermore, partial removal can be carried out at incremental steps leaving a distinct number of bilayers behind. The underlying nonlinear dependence of the patterning process on the laser intensity is traced back to the interplay between the laser-induced transient local temperature rise and the thermally activated desorption of the phospholipid molecules. Generally, the lateral resolution in photothermal processing depends on the thermal and chemical stability of the coating. Phospholipid films, of course, are soft supramolecular assemblies. Despite their soft nature, however, the collective interactions are quite strong. This gives rise to a strong nonlinearity as observed here. Considering these features, photothermal laser processing constitutes a powerful tool for micro- and nanopatterning of phospholipid films.

1. A. Terheiden, C. Mayer, K. Moh, B. Stahlmecke, S. Stappert, M. Acet, B. Rellinghaus, Appl. Phys. Lett. 84 (2004) 3891.
2. D. Dahlhaus, S. Franzka, E. Hasselbrink, N. Hartmann, Nano Lett. 6 (2006) 2358.
3. M. Mathieu, D. Schunk, S. Franzka, C. Mayer, E. Hasselbrink, N. Hartmann, Small, accepted.

3:40pm **BI+AS+NS-ThA6 The Role of Liposomes in Fluorescent Based Microarrays: From Surface Immobilization of Membrane Proteins to Highly Fluorescent Labels**

M. Bally, ETH and University Zurich, Switzerland*, K. Bailey,* CSIRO, Australia*, S. Syed, S. Buergel, J. Voeroes*, ETH and University Zurich, Switzerland

Technologies utilizing arrays of immobilized biomolecules on planar surfaces are emerging as powerful high throughput tools for bioanalytical measurements. Nowadays, optical sensors based on fluorescence detection are the most widespread. However, many applications especially in the area of protein sensing, rely on the availability of optimized sensing interfaces and signal amplification strategies. Liposomes, due to their hollow particle-like structure and their unique chemical and physical properties, have greatly contributed to the development of sensitive and accurate biological assays.

In this presentation, we highlight with results obtained recently, the contributions of phospholipid vesicles to the development of high performance fluorescence based biosensors.

First, liposomes are an optimal platform for the surface immobilization of membrane proteins since they provide the natural environment required for the functional surface immobilization of these fragile molecules. We demonstrate the creation of a functional, heterogeneous array of G-protein coupled receptors. Vesicles obtained from cellular membrane extracts containing either the H1R-histamine receptor or the M2R-muscarinic receptors were immobilized on a conventional oligonucleotide microarray via complementary tags. Fluorescent ligand binding assays were then performed illustrating that the receptors kept their native conformation. As an alternative platform, we introduce a novel approach for the creation of vesicle multilayers using zirconium phosphate chemistry. As demonstrated in a model biomolecular binding assay, such three dimensional constructs increase the protein loading capacity of a sensor surface.

Liposomes are also excellent candidates as labels for biological assays: phosphocholine-based vesicles are non-fouling and biomolecules or marker molecules (e.g. fluorophores or enzymes) can be easily attached to their surface or encapsulated in their inner cavity. We show that fluorescently labeled phospholipid vesicles provide simple and cheap means for signal amplification and sensitive protein detection on a microarray format. Using vesicles, up to 100 fold increase in sensitivity was observed in a model protein microarray with confocal read-out, compared to a conventional assay performed with fluorophore labeled antibodies.

The various approaches presented here will contribute to the development of sensitive and high performance microarrays for a variety of applications including the investigation of membrane proteins.

4:00pm **BI+AS+NS-ThA7 Fusion of Biomimetic 'Stealth' Probes into Lipid Bilayer Cores**

B. Almquist*, N. Melosh*, Stanford University

The ability to specifically and non-destructively incorporate inorganic structures into or through biological membranes is essential to realizing full bio-inorganic integration, such as arrayed on-chip patch-clamps, drug delivery, and biosensors. However, molecular delivery and interfaces to inorganic objects, such as patch-clamp pipettes, generally rely upon destructive formation of membrane holes and serendipitous adhesion, rather than selective penetration and attachment to the bilayer. In fact, materials greater than a few nanometers in size have not been shown to penetrate lipid bilayers without disrupting the continuity of the membrane. In this talk, I will discuss the development of nanofabricated probes that spontaneously insert into the hydrophobic membrane core by mimicking the hydrophobic banding of transmembrane proteins, forming a well-defined bio-inorganic lateral junction. These biomimetic 'stealth' probes consist of hydrophilic posts with 2-10 nm hydrophobic bands formed by molecular self-assembly, and are easily fabricated onto a variety of substrates including silicon wafers, nanoparticles, and atomic force microscope (AFM) tips.

By fabricating this architecture onto AFM probes, we have directly measured the penetration behavior and adhesion force of different molecular functionalities within the bilayer. It has been found that following insertion, the stealth probes remain anchored in the center of the bilayer, while purely hydrophilic probes have no preferred location. The strength of the stealth probe adhesion varies greatly between short and long chain alkane functionalizations, indicating that chain mobility, orientation, and hydrophobicity all contribute to molecular stability within the bilayer. In addition, the consequences of geometric factors such as band thickness and the presence of multiple bands on interface stability have been established. By selectively choosing the desired properties of the hydrophobic band, it will be shown that it is possible to tune the failure tension of the interface from values comparable to that of pristine lipid vesicles to only a fraction of the strength. Finally, the ability to transfer the stealth probe behavior to other platforms (e.g. nanoparticles for drug delivery) will be discussed.

4:20pm **BI+AS+NS-ThA8 Seeing Nanopore-spanning Supported Lipid Bilayers**

K. Kumar*, S. Kaufmann, M. Textor, E.O. Reimhult*, ETH Zurich, Switzerland

Supported lipid bilayers (SLBs) present a highly interesting cell-membrane-like format to study sensitive ion channels or other membrane proteins. If formed by the rupture of liposomes, they then have the major advantage over other planar membrane architectures for biosensing in that they can be formed completely bereft of organic solvents by self-assembly, enabling the further incorporation of the aforementioned sensitive membrane proteins.[1] Porous structures allow the use of fusogenic surfaces which enhance the formation of SLBs from liposomes, while accommodating the incorporation of larger membrane proteins by decoupling them from the surface. We have developed a particle lithography process to produce high aspect ratio pores with a diameter tunable between 40 nm and 200 nm into silicon nitride, silicon oxide or titanium oxide to take advantage of a range of different surface chemistries. SLBs were formed on these porous substrates and characterized by fluorescence and force microscopy. These results suggest that the underlying nanotopography of the substrate plays a major role in both the formation and characterisation of nanopore-SLBs. The outcome of liposome adsorption is strongly influenced by roughness features in the same size range as the liposomes, which has important implications for the reproducible formation and characterization of nanopore-spanning planar lipid membranes necessary for future applications in integrated membrane-based sensing.

1. Reimhult, E. and K. Kumar, Trends in Biotechnology, 2008. 26(2): p. 82-89.

4:40pm **BI+AS+NS-ThA9 Formation of Protein Surface Patterns by Ligand Self-Selection *from Mixed Protein Solutions***, *M. Dubey,* University of Washington, *K. Emoto,* Great Basin Scientific, *H. Takahashi, D.W. Grainger,* University of Utah, ***D.G. Castner***, University of Washington

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has been shown to be very sensitive for surface analysis and has been very useful for trace element detection. With the advent of improved analyzers, imaging ToF-SIMS provides spatial distribution of different species and helps in plotting the surface reactivity maps. Use of multivariate analysis, especially Principal Component Analysis (PCA) makes this technique even more powerful by differentiating regions with different chemistries. ToF-SIMS and PCA has been used in this work to study a very important two component patterned chemistry, which can have applications in bio-chips and cell-based biosensors. The chemistry is based on n-hydroxysuccinimide (NHS) esters; these molecules are widely used as leaving groups to activate covalent coupling of amine-containing biomolecules onto surfaces. The present work utilizes our knowledge of a previously studied model system, where NHS molecules were self-assembled on a gold substrate, and XPS and ToF-SIMS was used to characterize and understand the effect of hydrolysis and regeneration. We have demonstrated the extension of this chemistry to a commercial poly(ethylene glycol) (PEG)-based polymer films coated on glass slides. NHS and methoxy-capped regions were co-patterned onto these slides using photolithographic methods; then imaged with ToF-SIMS/PCA. NHS surface reactive zones are clearly resolved at high sensitivity despite the complexity of the matrix chemistry. Surface-specific protein coupling was observed by surface-selective reaction of streptavidin with the NHS patterns. The next step involved the preparation of photolithographic patterns of two affinity ligands (biotin and chloroalkane) for the specific immobilization of two different proteins (Streptavidin and HaloTag®). Spontaneous formation of high-fidelity surface patterns of the two proteins from their mixed solution was observed and characterized. In addition to Streptavidin and HaloTag®, ToF-SIMS detected the presence of non-specific BSA adsorption, a masking protein present in excess in the protein solutions, onto the patterned surfaces. ToF-SIMS amino acid-derived ion fragment yields summed to produce surface images can reliably determine which patterned surface regions contain bound proteins, but do not readily discriminate between different co-planar protein regions. However PCA of the ToF-SIMS data, improves discrimination of ions specific to each protein, facilitating surface pattern discrimination based on protein type. Also, ToF-SIMS imaging detected regions where residue from incompletely removed UV-exposed photoresist was present and its influence on protein adsorption.

5:00pm **BI+AS+NS-ThA10 Fabrication of Protein Patterns by Direct Electron-Beam Writing in a Protein-Repelling Template**, *N. Ballav,* Universität Heidelberg, Germany, *H. Thomas, T. Winkler, A. Terfort,* Goethe-Universität Frankfurt, Germany, ***M. Zharnikov***, Universität Heidelberg, Germany

One of the challenges of modern nanotechnology is the development of reliable, efficient, and flexible methods for the fabrication of ordered and complex patterns comprised of different proteins. An essential element of almost all available approaches is a protein-repelling "background" matrix, surrounding the active protein-adsorbing areas – the matrix prevents adsorption of proteins beyond these areas. Such a matrix is usually comprised of oligo- or poly(ethylene glycol)-based materials and is generally prepared by a backfilling procedure after the fabrication of the protein-attracting patterns. We present an alternative approach, showing that the protein-repelling matrix, both SAM- and polymer-like, can be used as a primary template for *direct* electron-beam writing of both *non-specific* and *specific* protein patterns of *any desirable shape*, including gradient ones, on a flexible length scale. The above factors make the approach quite versatile, which is additionally strengthened by intrinsic flexibility of electron-beam lithography, a wide range of suitable electron energies, broad availability of commercial oligoethylene glycol compounds, variable substrate material, and flexible choice of the target proteins. Complex gradient patterns fabricated by the suggested approach can become an important tool for mimicking natural biological interfaces which frequently possess gradient character – a typical way of encoding and displaying directional biological information.

BioMEMS Focus Topic
Room: A8 - Session BM+MN+MS+TF+BI-ThA

Advances in Microfluidics for BioMEMS
Moderator: G.W. Rubloff, University of Maryland

2:00pm **BM+MN+MS+TF+BI-ThA1 Advances towards Programmable Matter**, ***D. Erickson***, Cornell University **INVITED**

A dichotomy exists between the bottom-up self-assembly paradigm used to create regular structures at the nanoscale, and top-down approaches used to fabricate arbitrary structures serially at larger scales. The former of these enables rapid, highly parallel assembly but lacks critically important features of the latter such as the ability to arbitrarily direct the assembly location and perform error correction. We and our collaborators have recently proposed an alternative approach which combines these two based on dynamically programmable self-assembling materials, or ***programmable matter***. The uniqueness of our approach is that it uses dynamically-switchable affinities between assembling components facilitating the assembly of irregular structures. In this talk I present an overview of our approach and detail some of the analytical and experimental advances towards a programmable matter system we have recently made. These include: the development of a multi-chamber microfluidic chip for improved far-field assembly, the demonstration of near-field inter-tile affinity switching using a thermorheological assembly fluid and the ability to enhance assembly in three dimensions using unique fluid-structure interactions.

2:40pm **BM+MN+MS+TF+BI-ThA3 A Multilayered Microfluidic System with Buried Channels and Cell Compartmentalization for Engineering Heterogeneous Neural Networks**, *C. James, A. Greene,* ***A. Schiess***, *G. Bachand,* Sandia National Laboratories, *M. Romero-Ortega*, University of Texas at Arlington

Current technology for engineering *in vitro* neural networks utilizes cell guidance cues that yield only temporary networks (< 1 month) as the cells rapidly diverge from their designed guidance cues during development of the culture. In addition, these engineered networks are typically comprised of homogeneous populations of neurons, thus the lack of multiple neuron types produces oversimplified networks that do not adequately represent in vivo networks. In addition, effective control over synaptic connections between different populations of neurons has not been demonstrated. Here, we describe a novel hybrid technology of multi-layered microfluidics with compartmentalized chambers containing multiple neuron types for engineering robust and complex neural networks with high resolution organization of synaptic connections. The device contains a first level of microfluidic channels etched 1-2 microns into the base glass substrate. These channels are fabricated with a novel process using a silicon nitride mask for hydrofluoric acid undercut etching to create buried microfluidic channels for robust containment and guidance of neurons. After the etching process, photoresist liftoff is performed to selectively adsorb poly-L-lysine (PLL) within the buried channels for improved neuron attachment and outgrowth at pre-defined locations. Polarity control of neurons is provided through a continuous set of guidance cues to promote axon development, while interrupted sets of guidance cues promote dendrite development. Current results show that axons and dendrites are positioned at predefined locations with a >65% accuracy. A second level of microfluidic channels and large (~mm) cell chambers are fabricated in polydimethylsiloxane (PDMS) from two-level SU-8 master molds. The base glass substrate and the PDMS substrate are aligned and bonded to create interconnects between channels in both substrates. These interconnects provide interaction regions for the development of synapses between growing neurites from cells in different chambers. We are currently applying this technology to engineer corticostriatal networks, an important region of the brain responsible for integrating multiple informational inputs crucial to complex decision-making in higher mammals. Specifically, we are using patch-clamp electrophysiology to track the development of synaptic memory in the form of long-term depression and potentiation (LTD/LTP) in these engineered networks.

3:00pm **BM+MN+MS+TF+BI-ThA4 Vesicle Production on a Microfluidic Platform using pH Sensitive Block Copolymers**, ***L.E. Brown***, The University of Sheffield, UK, *S.L. McArthur*, Swinburne University of Technology, Australia, *G. Battaglia, P.C. Wright*, The University of Sheffield, UK

The development of pH sensitive, biocompatible block copolymer vesicles has enabled the intracellular delivery of water soluble drugs and proteins. Improving the encapsulation efficiency of the vesicles is now a critical parameter. Transferring the production method to a microfluidic device creates the potential to vary the encapsulation conditions and improve this efficiency. In this work, a flow focussing microfluidic device is used. The self assembly of PMPC-b-PDPA block copolymer vesicles is induced within the device by changing the pH of the flows within the microchannels. The use of pH shift eliminates the need for organic solvents currently required for glass capillary production methods. This enables the biocompatibility of the block copolymers to be maintained, an essential factor for their application as molecular delivery vehicles.

The flow focussing microfluidic device was produced through standard soft lithography techniques. A three-channel flow system is used with the copolymer in solution at pH6 in the central channel and aqueous buffered solutions flowing in the channels either side. The laminar flow conditions within the microfluidic device result in a pH gradient at the interfaces where the three channels meet and where the block copolymers self-assemble into vesicles. These vesicle formation processes have been imaged using confocal microscopy via FRET with a block copolymer containing both rhodamine and fluorescein isothiocyanate groups. Dynamic light scattering and TEM were used to confirm vesicle formation.

With 50nm to 250nm vesicles continuously being produced within the device it was then possible to investigate whether higher encapsulation efficiencies can be achieved using the microfluidic device. The protein myoglobin was introduced through the central channel along with the copolymer. Spectrophotometric analysis indicated the overall the efficiency of the encapsulation process within the device is not a significant improvement on the standard bulk methods currently used, involving sonication of the vesicle solution containing the molecule to be encapsulated. Despite this, the continuous nature of microfluidic devices, as well as the lack of organic solvents being used in the production process indicates that the development of these devices offers a viable alternative production method for polymer vesicles that may enable the increases in encapsulation efficiency to be achieved. Work is ongoing to achieve this using the same pH shift mechanism within a glass capillary microfluidic device.

3:40pm **BM+MN+MS+TF+BI-ThA6 Integration of a Microfluidic Flow Cell Array with SPR Microscopy for In Situ Microarray Formation and Biomolecule Interaction Analysis**, *J. Liu, M. Eddings,* University of Utah, *A. Miles,* Wasatch Microfluidics, *B. Gale,* ***J. Shumaker-Parry***, University of Utah

Analysis of biomolecule interactions based on surface plasmon resonance (SPR) microscopy provides a label-free approach to monitoring arrays of biomolecule interactions in real time. Typically the microarray sensing surface for these measurements is prepared ex situ and a single or few channel flow cell is used for the biomolecule interaction studies. The multiplexing nature then is derived from the microarray and the number of samples that can be run simultaneously is rather limited, diminishing the potential application for assays requiring a high-throughput approach due to a large number of samples. One example of this is the need to monitor for anti-drug antibodies from a large pool of patient samples during clinical trials of biotherapeutics. We demonstrate the capability of a multi-channel microfluidic flow cell array (MFCA) to expand the throughput capability when integrated with SPR microscopy. In addition, the MFCA provides an in situ approach to array fabrication that allows full characterization of the biomolecule immobilization process. We use the MFCA for delivery of sample solutions with continuous flow in 48 channels in parallel for rapid microarray creation and binding analysis while using SPR microscopy for real-time monitoring of these processes. Label-free measurement of antibody-antibody interactions demonstrates the capabilities of the integrated MFCA-SPR microscopy system and establishes the first steps of the development of a high-throughput, label-free immunogenicity assay. We demonstrate a limit of detection (LOD) of ~ 80 ng/ml for the particular antibody pair we studied. This LOD is ~6 times lower than the industry recommended immunogenicity assay detection limit. The high-throughput nature of the integrated system allows a large number of replicate experiments, including control experiments, to be performed simultaneously on the same sensor surface in a short time. The integrated system also will be applicable for more general high-throughput protein-array based analysis.

4:20pm **BM+MN+MS+TF+BI-ThA8 Nanochannel Stretching of Nucleic Acids: Towards Epigenetic Analysis**, *D.E. Streng, S.-F. Lim, A. Karpusenka, J. Pan, J.A. Hook,* ***R. Riehn***, NC State University

Nanochannels with a diameter of about 100nm2 are a novel method for stretching DNA for genomic investigations. Such devices are implemented through standard nanolithography in fused silica. The elongation of DNA results from an interplay of steric and entropic effects. Previous applications of nanochannel stretching included sizing, restriction mapping, and observation of transcription factor binding.

We show here that nanochannels can also be used to map the site-specific epigenetic state of DNA. In particular, we show here that the concept by nanoconfinement can be extended to chromatin, or DNA complexed to histones, and that the stretching is within the range expected from the de Gennes theory. We also demonstrate that the location-resolved cytidine methylation state of DNA can be mapped by specific fluorescent labeling. We will discuss the basic operation of these technique, and the application to artificial substrates with predefined epigenetic marks.

4:40pm **BM+MN+MS+TF+BI-ThA9 Microfluidic Models of Endothelial Cell Sprouting in Response to Biomechanical and Biochemical Microenvironments**, ***A.M. Shamloo***, *S.C. Heilshorn*, Stanford University

A novel microfluidic device was designed in order to generate stable, quantifiable concentration gradients of biomolecules in a cell culture chamber for 2-D and 3-D studies of shear-sensitive cell types such as endothelial cells. Endothelial cells form the inner lining of blood vessels and initiate a critical step in angiogenesis (the sprouting of new blood vessels) during wound healing and cancerous tumor growth. Therefore, a deeper understanding of the critical biomechanical and biochemical factors regulating endothelial cell sprouting can lead to improved clinical therapies for a multitude of diseases. Concentration distribution of soluble growth factors inside the microfluidic cell culture chamber was determined by simulation and experiment, and the stability of the gradient was verified over multiple hours. This device allows independent tuning of the matrix rigidity, the growth factor absolute concentration, and the growth factor concentration gradient steepness within a single experimental platform. Sprout formation of dermal microvascular endothelial cells was studied within collagen gels of varying density (0.3 - 2.7 mg/mL, corresponding to shear moduli of 8 – 800 Pa) that contained stable gradients of soluble vascular endothelial growth factor (VEGF). These experiments revealed that endothelial sprouting into multi-cellular, capillary-like structures is optimized at an intermediate collagen matrix density (G'~100 Pa). At lower matrix densities, cells were more likely to lose their coordinated motion and migrate as individual cells through the matrix; while at higher matrix densities, the cells formed broad cell clusters that rarely elongated into a sprout. Sprout thickness directly correlated with matrix rigidity, with thicker and less frequent sprouts present in gels with the highest shear moduli. Intriguingly, our 3D experiments also found that endothelial sprouts alter their sensitivity to VEGF depending on the matrix density, suggesting a complex interplay between biochemical and biomechanical factors. As matrix stiffness increases, steeper VEGF gradients and higher VEGF absolute concentrations are required to induce directional sprouting. In more compliant gels, endothelial sprouts that originally misaligned were able to turn and properly reorient parallel to the VEGF gradient; however, this turning phenomenon was only rarely observed in stiffer gels. These results demonstrate that matrix stiffness is an effective factor in stabilization and orientation of endothelial cells during sprouting and suggests new anti-angiogenic strategies for potential cancer treatment as well as pro-angiogenic strategies for regenerative medicine scaffolds.

5:00pm **BM+MN+MS+TF+BI-ThA10 Plasma Polymerisation of PDMS for Microfluidic Applications**, ***S. Forster***, *A.G. Pereira-Medrano, G. Battaglia, P.C. Wright,* University of Sheffield, UK, *S.L. McArthur*, Swinburne University of Technology, Australia

Polydimethylsiloxane (PDMS) has become the most popular material choice for a wide range of microfluidic bioengineering applications, including proteomics, protein separations and drug discovery and development. The reasons its popularity lie mainly in its highly advantageous fabrication requirements when compared to traditional materials such as glass and silicon. However, PDMS has some fundamental drawbacks, namely a lack of functionality present at the surface, high protein fouling and an 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. Due to this reason much work has been completed looking into surface modification of PDMS for such applications. Here an alternative method of stable surface modification of PDMS for many microfluidic applications through enhanced curing conditions and plasma polymerisation is shown. Stable and functional surface coatings have been achieved on bulk PDMS and within microfluidic channels. Bulk surfaces were characterised using a combination of XPS and

ToF-SIMS, while coated micro-channels were tested using confocal microscopy and various assays. This methodology has been used in many applications and one area where it has proven extremely useful is in microfluidic proteomics where surface properties are of paramount importance due to the inherently small volumes and quantities associated with biological samples. Firstly, plasma polymer coated PDMS micro-channels were utilised for on-chip IEF protein separations (i.e. separating proteins bases on charge) and showed reduced electrosmotic flow (EOF) and protein adsorption within the device. Secondly, a µIMER (micro-immobilised enzyme reactor) was produced using plasma polymer coated PDMS devices. The µIMER was then used in 'shotgun' protein digestion applications in conjunction with Mass Spectrometry where it was shown to have numerous advantages over untreated PDMS devices, as well as comparing favorably to published work on other µIMER systems. The device was used to digest single and multiple protein samples as well as complex membrane protein samples. Finally, successful covalent bonding of plasma polymer coated devices has led to the completion of polymer vesicle immobilisation within a microfluidic channel. Initial work looking at the immobilisation of polymer vesicles with an encapsulated digestive enzyme has shown to increase proteomic digestion efficiency. This success opens up the possibility of translating this technique into many potential microfluidic applications through the extensive versatility of encapsulation within polymer vesicles.

Electronic Materials and Processing
Room: B1 - Session EM-ThA

Quantum Structures and Nitrides Devices
Moderator: F. Ren, University of Florida

2:00pm **EM-ThA1 Filling of Few Electron Quantum Dots Imaged and Characterized By Scanning Force Microscopy**, ***L.P. Cockins***, *Y. Miyahara, S.D. Bennett, A.A. Clerk,* McGill University, Canada, *S. Studenikin, P. Poole, A. Sachrajda,* National Research Council, Canada, *P. Grutter*, McGill University, Canada

The ability of quantum dots to confine single charges at discrete energy levels makes them a promising platform for quantum computation where the intrinsic properties of single electrons, such as spin, act as the conventional 1 and 0 bit in a classical computer. In order to control initialization and to scale up the number of bits, an understanding of both the energy levels of single quantum dots and the variation between dots need to be characterized.

Self assembled quantum dots are of considerable interest in this field because their size, shape, and material can be controlled during the growth process. Controlling these properties is important as these influence the confinement potential, thereby controlling the energy levels of the dot. However, the method of growth makes positioning of the quantum dots difficult and usually they are randomly distributed over the sample surface. This, in addition to the small size of the dot, makes it challenging for lithography techniques to access the quantum dots to perform either charge transport or charge sensing measurements so that the dot properties can be measured.

An atomic force microscope can be used to spatially access the dots, and by applying a voltage between cantilever tip and back-electrode (beneath the dot), the energy levels of individual dots can be probed. At low temperatures the dots are in the Coulomb blockade regime and individual electrons can be controllably added by applying a sufficient bias voltage to overcome this electrostatic repulsive energy. The oscillating cantilever in these experiments is responsible for both loading/emptying the dots through electrical gating and also detecting tunneling events through a change in resonant frequency and/or the amount of energy required to maintain a constant oscillation amplitude. Electrical leads are not required in this experiment which not only leaves the surface electrostatically intact but also gives us the freedom to investigate any dot on the surface.

Using an atomic force microscope we demonstrate the ability to probe the energy levels in few electron self assembled InAs quantum dots. The charging energy, level spacing, and shell structure of single dots are extracted and supported theoretically. Multi-dot complexes are also investigated and pairs of dots which are either capacitively or tunnel coupled are observed. Increasing the oscillation amplitude of the cantilever allows for the additional electron to enter the dot at a higher energy level, in a way probing the excited states of the dot similar to excited state spectroscopy. These findings are also supported by theoretically.

2:20pm **EM-ThA2 InAs Lateral Quantum Dot Molecules with Controllable Configurations**, ***M.K. Yakes***, *A.S. Bracker, C.D. Cress, J.G. Tischler, D. Kim, A. Greilich, D. Gammon, A.R. Laracuente*, Naval Research Laboratory

A quantum dot molecule (QDM) is formed when two or more quantum dots are close enough so that the electronic properties of each dot are affected by the presence of the other. Well controlled, vertically-stacked QDMs are now routinely grown for optical investigations.[1] [#_ftn1] For device applications, laterally coupled dots offer compatibility with existing gate technologies and advantages in scalability. However, growth of complex laterally coupled QDMs is more challenging than the vertically stacked dots.

One method for influencing the lateral position of self-assembled QDs is to introduce features on the substrate which will act as preferred nucleation sites for dot growth.[2] [#_ftn2] One promising technique is to use gallium droplet epitaxy to form a template for further dot growth. In droplet epitaxy, gallium is deposited without arsenic overpressure, forming metallic islands without a wetting layer. When these droplets are exposed to arsenic and annealed they crystallize into homoepitaxial mounds. When InAs is grown on these mounds, the islands appear to grow only on the sloping edges of these mounds. Previous structures grown with this technique have demonstrated flexibility in QDM configuration and excellent uniformity.[3] [#_ftn3]

In this presentation, we will describe new growth techniques that can be used to control the configurations of lateral InAs QDMs. By fixing the direction of the incident indium flux, the indium beam is shadowed by the GaAs mounds, so that InAs dots will only form on the sides of the mound which face the indium source. This allows new configurations of QDMs to be grown that cannot be formed using a rotating substrate. In addition, by capping first layer QDMs with GaAs or AlGaAs and growing additional strain-coupled dots, we demonstrate flexible and uniform three dimensional QDM configurations.

With atomic force microscopy it is not possible to determine the structure of the InAs dots once they are buried under a GaAs capping layer. Cross sectional scanning tunneling microscopy (XSTM) is an ideal technique to examine the final structure with atomic resolution. For bi-molecules, the interdot separation is 8 nm and the center to center distance is 30 nm, which makes them excellent candidates for investigations of electron tunneling using photoluminescence spectroscopy.

---

[1] [#_ftnref1] E. Stinaff *et al., Science* **311** 636 (2006)

[2] [#_ftnref2] R. Songmuang *et al., Appl Phys Lett* **82** 2892 (2003)

[3] [#_ftnref3] J.H. Lee *et al., Appl Phys Lett* **89** 202101 (2006)

2:40pm **EM-ThA3 MBE Growth and Optical Properties of GaN Quantum Structures**, ***N. Grandjean***, Ecole Polytechnique Fédérale de Lausanne (EPFL), Switzerland **INVITED**

In this presentation, we will first address the fabrication of III-V nitride based quantum dots (QDs) using molecular beam epitaxy with ammonia as nitrogen source. We will focus on strain-induced Stranski-Krastanov (SK) growth mode in GaN/AlN system and point out the effect of surface free-energy. It is indeed observed that the V/III ratio controls the 3D island formation in a reversible way. In a second part, we will discuss the optical properties of an ensemble of GaN/AlN QDs. Photoluminescence experiments evidence that the transition energies are dominated by a giant quantum confined Stark effect, which results from the presence of a huge built-in electric field of several MV/cm. This electric field is inherent to wurtzite III-nitride based heterostructures when they are grown along a polar axis. It comes from spontaneous and piezoelectric polarization discontinuities arising at interfaces between different materials. Then, mesa are prepared aimed at single dot spectroscopy using micro-photoluminescence. Optical signatures of excitons and bi-excitons are clearly seen on the luminescence spectra. Both positive and negative binding energies are deduced depending on the dot size. A phenomenological model including the built-in electric field present in the dots well accounts for the experimental observations.

3:40pm **EM-ThA6 Growth and Process Technologies for High Efficiency InGaN-Based Light-Emitting Diodes**, ***J.-I. Chyi***, *H.-C. Lin*, National Central University, Taiwan **INVITED**

Raising external quantum efficiency has always been the focused area of research in InGaN blue/green light-emitting diodes (LEDs). In the early 90s, breakthroughs in material growth and p-type doping restored the heat of pursuing high brightness InGaN LEDs. It was, however, several other key technology advancements that made solid-state lighting era a reality. Among these technologies, patterning sapphire substrate and semiconductor surface is one of the most essential one. In this report, we present three different patterning techniques, which emphasize different aspects of patterning technology and show how they impact the external quantum efficiency as well as other characteristics of InGaN/GaN quantum well light-emitting diodes. We report the epitaxial growth of GaN on patterned sapphire substrates (PSSs) with micro-lens of three different geometric shapes by metal-organic chemical vapor deposition. Growth mode analysis shows that micro-lens with sharp tips prohibit the nucleation and growth of GaN on their top and lead to a wider lateral growth region with low dislocation density. The external quantum efficiency (at 20 mA) of LEDs is improved by nearly 20% by using this technique. However, the residual strain instead of dislocation density in the GaN buffer layer plays a heavier role in the external quantum efficiency of the light-emitting diodes. Although the PSS approach has been shown effective and gives the freedom of pattern design, it requires extra photolithographic steps that make it more complicated and costly. We propose a maskless wet-etching method to prepare patterned sapphire substrates, namely naturally etched sapphire substrates (NESSs). At 20 mA, nearly 20% improvement in external quantum efficiency is achieved even the LEDs have already an indium-tin oxide transparent contact layer and a roughened surface. It has also been shown that the uniformity of device performance across the wafer is not a concern when using this technique. The surface patterning techniques reported so far involve spatially with the active region of LEDs and make the patterning process very critical in maintaining device performance as well as reliability. To avoid this problem, we propose to pattern the dicing streets around the LED chips where no electrical contacts are present. Forming a triangular lattice consisting of dry-etched circular holes with a diameter/periodicity of 3/3 μm on the dicing street. The external quantum efficiency (at 20 mA) of the LEDs is increased by about 13%. Meanwhile, the forward voltage increases only 0.05 V and improved reliability is observed as expected. In addition, a novel growth technique for improving internal quantum efficiency will also be presented. During the growth of quantum wells, a growth interruption is introduced at each InGaN to GaN interface while having trimethylindium (TMIn) and NH3 continue flowing into the reactor. Photoluminescence, X-ray diffraction, atom force microscopy, and high-resolution transmission electron microscopy indicate that the treatment leads to a smoother InGaN surface and InGaN/GaN interface with substantial decrease in V-shape defects density, compared to the samples without the treatment. The external quantum efficiency of 525 nm green LEDs prepared by this process is increased by as much as 43%.

4:40pm **EM-ThA9 ENABLE-Based Growth of In-Rich InGaN for Photovoltaic and Light-Emitting-Diode Devices**

***T.L. Williamson**, M.A. Hoffbauer,* Los Alamos National Laboratory*, K.M. Yu, L.A. Reichertz, N. Miller, J.W. Ager, W. Walukiewicz*, Lawrence Berkeley National Lab

A wide range of photovoltaic (PV) and light-emitting-diode (LED) devices can be made utilizing the wide band gap tunability of InxGa1-xN (0.7 eV to 3.4 eV, 1>x>0). Growing In-rich InxGa1-xN films with strong photoluminescence in the green and red portions of the visible spectrum has faced considerable challenges due to In segregation and other materials issues. These challenges have precluded the growth of both compositionally graded InxGa1-xN materials and higher bandgap Ga-rich materials on top of lower bandgap In-rich materials. Overcoming these difficulties has proved formidable for conventional epitaxial techniques due to the low decomposition temperatures of In-rich materials (e.g. InN~550°C) and the required growth temperatures for Ga-rich materials (e.g. GaN >800°C).

Energetic neutral atom beam lithography & epitaxy (ENABLE) is a recently developed low-temperature thin film growth technology developed at LANL that utilizes a collimated beam of energetic neutral N atoms (kinetic energies 0.5 to 5.0 eV) to react with evaporated Ga and In metals to grow InxGa1-xN. ENABLE is similar to MBE, but provides a much larger N atom flux. The high kinetic energy of the reactive N atoms substantially reduces the need for high substrate temperatures, making isothermal growth over the entire InxGa1-xN alloy composition range possible at rates of >3 mm/hr with no toxic precursors or waste products.

Current progress using ENABLE for growing InN, GaN, InxGa1-xN, and graded InxGa1-xN films over the full composition range will be presented including data on film photoluminescence, crystallinity, electrical properties, doping, and electroluminescence. ENABLE-grown InxGa1-xN films show strong photo- and electro-luminescence spanning the entire visible region of the spectrum, with carrier mobilities ranging from ~10 to >1400 cm2/Vsec and background carrier concentrations typically in the low 1017 range. Evidence for p-type doping of In-rich InxGa1-xN films and characterization of p/n junctions will be discussed along with the prospects for using ENABLE to fabricate efficient devices for PV and LED applications.

5:00pm **EM-ThA10 Self-annealing Effect in Neutron-Irradiated AlGaN/GaN High Electron Mobility Transistors**

G. Ko*,* Korea University, South Korea*, F. Ren, S.J. Pearton,* University of Florida*, J. Kim, H.-Y. Kim*, Korea University, South Korea

AlGaN/GAN High Electron Mobility Transistors (HEMTs) have been studied due to their chemical and physical stability under harsh environments as well as high power and high frequency applications. Especially, AlGaN/GaN HEMT is considered as the potential candidate for space-based systems such as the space shuttles and the satellites. It is empirically known that displacement threshold energy (E_d) which is the energy required to displace an atom from its lattice position is inversely proportional to lattice constants. Since the lattice constant of GaN (a = 3.2496 Å) is smaller than Si (5.4301 Å) or GaAs (5.6533 Å), its radiation hardness is much better than these. Since neutron-induced effects on AlGaN/GaN heterostructures are not well known. We investigated self-annealing effect occurred in low-dose ($< 10^{12}$ cm^{-2}) neutron-irradiated AlGaN/GaN HEMT at room temperature. The device structure consisted of 25 nm AlGaN with 50 nm GaN cap layer on undoped 2 um GaN. These layers were grown on AlN buffer layer and c-plane sapphire by MOCVD. Ohmic metal was Ti/Al/Ni/Au and gate metal was Ni/Au. Neutron irradiation was performed with MC-50 cyclotron at Korea Institute of Radiological and Medical Sciences. Neutrons were generated when 35MeV protons collided with beryllium target occurring nuclear reaction. The average neutron energy was 9.8 MeV and the total fluence was 5.49×10^{11} cm^{-2}. Electrical properties (V_{ds}-I_{ds}, V_{gs}-I_{gs}, and transconductance) had been measured during 30 days after neutron irradiation. We could observe V_{ds}-I_{ds} drastically decrease for 7 days, which meant surface traps and deep traps were created in AlGaN/GaN HEMT. However its current level was gradually recovered after 7 days. And the recovery of transconductance and leakage current were also confirmed. This self-annealing effect can be attributed to the recombination of the created defects because the distance between the neighboring defects is very short. The defect clusters that are mobile at room temperature were created by neutron irradiation. The details about the irradiation and self-annealing will be presented.

5:20pm **EM-ThA11 Engineering Epitaxial AlN Thin Films on Wide Bandgap Semiconductors**

***Y.-C. Perng**, J. Chang*, University of California, Los Angeles

Wide bandgap semiconductors have been interesting for high temperatures operation and serving as materials using in high power and RF devices because of their high breakdown voltages. Aluminum nitride, a wide bandgap material (6.2 eV), is a promising interfacial layer or dielectric material on wide bandgap semiconductors, especially SiC and AlxGa1-xN/GaN. Because of its small lattice mismatch to SiC and AlxGa1-xN/GaN (1.3% and <2%)1 and a similar thermal expansion coefficient, it could potentially lower the interface state densities between the materials. Conventionally, AlN thin films are deposited by molecular beam epitaxy (MBE) on these wide bandgap materials. In this work, ALD is chosen to assess its ability to grow ultra-thin, uniform, and conformal AlN on these substrates, as a potential alternative for synthesizing epitaxial materials over a larger substrate and at lower temperatures.

Atomic layer deposition (ALD) has been utilized to synthesize AlN thin films by using trimethyl aluminum (TMA) and ammonia (NH3) as precursors at 400~500oC under high vacuum as 10-4~10-6 torr. The deposition rate of AlN on SiC and AlGaN were determined to be about 0.08nm/cycle. The composition, microstructure, and surface morphology were determined by x-ray photoelectron spectroscopy, transmission electron microscopy, x-ray diffraction and atomic force microscope. Fourier Transform infrared spectroscopy is implemented to study the change of surface functional groups during TMA and ammonia pulses, in an effort to affirm the mechanism leading to the growth of stoichiometric AlN. The as-deposited AlN was amorphous, as monitored by *in situ* by RHEED analysis but can be transformed into an epitaxial layer on SiC and AlGaN by a high temperature rapid thermal annealing process at 900oC. By synchrotron based XRD, we determined the epitaxial relationship between AlN and SiC to be AlN(11-20)||SiC(11-20) and AlN(0004)||SiC(0008). Similarly, the epitaxial relation to AlGaN is AlN(11-20)||AlGaN(11-20) and AlN(0002)||AlGaN(0002). Capacitance-voltage and conductance -voltage characteristics are used to determine the interface states density between the thin film and wide bandgap substrate. This process is also combined with an ALD Al2O3 process to synthesize aluminum oxinitride as a graded interfacial layer between AlN and Al2O3, to realize the fabrication and testing of viable MIS-HEMT structures.

1 H. Morkoc, S. Strite, G. B. Gao et al., Journal Of Applied Physics 76 (3), 1363 (1994).

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: C4 - Session IS+AS-ThA

In-Situ Microscopy and Spectroscopy: Surface Reactions
Moderator: P. Nachimuthu, Pacific Northwest National Laboratory

2:00pm **IS+AS-ThA1 Interface Science in Nanoparticles: An Electronic Structure View of Photon-in/Photon-out Soft-X-Ray Spectroscopy**, ***J.-H. Guo***, Lawrence Berkeley National Laboratory

Solar energy can be converted to electricity and chemical fuels for energy use and storage. However, the cost and conversion efficiency have been the biggest challenge for potential use of solar energy. There are the emerging technologies of using semiconductors for light harvesting assemblies; and charge transfer processes to solar cells. It could provide a significant contribution to our electrical and chemical resources if efficient and inexpensive systems utilizing readily available materials could be devised for the conversion process.

This presentation will shade some light on synchrotron radiation based soft-x-ray spectroscopy study of nanostructured materials. Soft-x-ray absorption probes the local *unoccupied* electronic structure (conduction band); soft-x-ray emission probes the *occupied* electronic structure (valence band); and the addition of resonant inelastic soft-x-ray scattering (Raman spectroscopy with soft x-rays) can tell the energy levels that reflect the chemical and physical properties of semiconductors. The experimental studies suggest that in-situ photon-in/photon-out soft-x-ray spectroscopy becomes an emerging tool for investigating the surface and interface science.

(1) The examples show quantum size effects on the exciton and band-gap energies of semiconductor nanocrystals (Hematite nanoarrays). Such finding strongly suggests that such designed nanomaterials could meet the bandgap requirement for the photocatalytic oxidation of water without an applied bias.

(2) The storage of hydrogen in a both safe and compact manner is of great importance for, for example, hydrogen powered vehicles. We have explored in-situ photon-in/photon-out soft-X-ray spectroscopy to study the molecular adsorption of H_2 on SWNTs under ambient pressures. The spectral changes with the increasing gas pressures provide the strong evidences for the tube-wall structure deformation and possibly a fraction of charge transfer due to the gas collision.

2:20pm **IS+AS-ThA2 In Situ GIXAFS and HERFD-XAS Studies of Pt-modified Rh(111) and Rh(221) Electrodes**, ***D. Friebel***, *D.J. Miller, H. Ogasawara, T. Anniyev, C.P. O'Grady, U. Bergmann, J. Bargar, A. Nilsson,* Stanford Synchrotron Radiation Lightsource*, K.T. Wikfeldt, L.G.M. Pettersson*, Stockholm University, Sweden

The oxygen reduction reaction at Pt electrodes has a high overpotential which drastically reduces the efficiency of fuel cells. The origin of the overpotential has been seen in the formation of stable Pt-O species at high potentials. Aiming at an unambiguous characterization of such Pt-O species, we use in situ grazing incidence x-ray absorption spectroscopy at the Pt L_3 edge to study the geometric and electronic structure of ultrathin Pt layers on Rh(111) and Rh(221) substrates as a function of the electrochemical potential. The use of Pt monolayers on a foreign metal substrate makes the bulk-penetrating hard x-ray probe surface sensitive and, furthermore, can be used for a variety of substrates to elucidate the influence of metal-metal interactions and interfacial strain on the catalytic activity of the Pt layer. The stepped Rh(221) surface serves as a well defined model substrate to study the influence of defects which are also expected to occur in nanoparticle catalysts.

We present our results from Pt L_3-edge grazing incidence x-ray absorption fine structure (GIXAFS) and high energy resolution fluorescence detection (HERFD) XAS measurements of an ultrathin Pt layer on Rh(111) in 0.01 M $HClO_4$ solution. The Pt layer was produced by UHV evaporation. In the HERFD-XAS experiment, we used a multi-crystal analyzer to reduce the core hole lifetime broadening. The high resolution spectra reveal additional spectral features of the near-edge region which can be theoretically modeled using the FEFF8 code and thus allow us to build an accurate structure model of the Pt/electrolyte interface.

2:40pm **IS+AS-ThA3 Chemical Imaging of Catalytic Solids at the Micron- and Nanoscale**, *B.M. Weckhuysen,* ***E. de Smit***, Utrecht University, the Netherlands **INVITED**

Most characterization studies of catalytic solids focus on ensemble-averaged measurements, assuming that catalytic solids are spatially homogeneous materials when placed in a reactor. Structure-performance relationships can then be obtained by relating activity and selectivity with a multitude of spectroscopic signatures. However, these signatures are not necessarily identical across e.g. a catalyst grain or fixed bed reactor. Detailed knowledge on these spatial heterogeneities is required to better understand reaction and deactivation mechanism. This keynote lecture discusses the potential of spectroscopic methods for chemical imaging spatial heterogeneities within catalytic solids at the micron- and nanoscale. Special emphasis will be on the use of in situ Scanning Transmission X-ray microscopy (STXM), UV-Vis microscopy, synchrotron IR microscopy, Coherent Anti-Stokes Raman Scattering (CARS) microscopy and (confocal) fluorescence microscopy. Two showcases will be discussed, namely Fe-based Fischer-Tropsch Synthesis (FTS) and H-ZSM-5 zeolites, catalyzing the oligomerisation of styrene and methanol to hydrocarbons. For the latter showcase, large coffin-shaped H-ZSM-5 crystals have been studied.

3:40pm **IS+AS-ThA6 Using Synchrotron Based in situ X-ray Techniques and TEM to Study Electrode Materials for Lithium Batteries**, ***X.Q. Yang***, Brookhaven National Laboratory **INVITED**

Recently, we have developed techniques using the combination of a high intensity synchrotron x-ray beam and fast detectors (image plate or position sensitive detectors) to do in-situ X-ray diffraction (XRD) during charge-discharge cycling and time resolved X-ray diffraction during the thermal decomposition of charged cathode materials. We have also developed synchrotron based in-situ X-ray absorption (XAS) techniques to study the changes of oxidation states and coordination of the transition metal elements during cycling. The in-situ and ex-situ soft x-ray absorption spectroscopy techniques we have developed allow us to distinguish the structural differences between the surface and bulk of electrodes using both electron yield (EY) and fluorescence yield (FY) detectors simultaneously. In this presentation, we will report our studies on the structural changes of various cathode materials such as layered LiMO2 (M=Co, Mn, Ni) and olivine structured LiMPO4 (M=Fe, Mn, Co, Ni) with and without surface coating, during charge-discharge cycling as well as during thermal decompositions. The results of these studies provide very important information for synthesizing new cathode materials with improved properties. Preliminary results of studies using in-situ transmission electron microscopy and high-resolution analyses will also be reported. ACKNOWLEDGMENT This work done at Brookhaven National Lab. was supported by the Assistant Secretary for Energy Efficiency and Renewable Energy, Office of Vehicle Technologies of the U.S. DOE under Contract No. DE-AC02-98CH10886

4:20pm **IS+AS-ThA8 Direct Observation of Interfacial Layer Formation in Li-Ion Battery using In-Situ TEM and EELS**, ***C.M. Wang***, *W. Xu, L. Saraf, B. Arey, J. Liu, Z. Yang, J.G. Zhang, S. Thevuthasan, D.R. Baer*, Pacific Northwest National Laboratory

One of the fundamental challenges facing the Li-ion battery development is the understanding of the fading mechanism of the active electrode materials during the repeated charging and discharging. In-situ methods based on x-rays have provided some information regarding the structural evolution of the electrode materials during the operation of a battery. However, in-situ work using x-ray only gives the average results, yielding no spatial resolution. Furthermore, it has been generally realized that the microstructural evolutions both at the interface between the electrolyte and the electrode and within the electrode (active materials) due to Li migration play a vital role on the performance as well as the overall life-cycle of the battery. In-situ transmission electron microscopy (TEM) and spectroscopy will be ideal tools for probing the structural evolution of the electrode materials during battery operation. However, related to the high vacuum operation of a TEM as well as the requirement of electron transmission through the sample, a prototype battery must be sealed with thin membrane that enables the electron transmission at the interested region. It is known that electrolytes based on ionic liquid have a low vapor pressure. Therefore, it is generally expected that using ionic liquid as electrolyte, the prototype battery may be operated in vacuum without sealing the whole system using a thin membrane. In this work, we report our exploratory work on developing in-situ TEM devices that will eventually enable direct and high spatial resolution observation of the structural evolution of the interface between the electrolyte and the electrode materials. In a model experiment, a prototype Li-ion battery was developed in the system of using SnO_2 nanowire as anode, an air stable salt LiTFSI in a hydrophobic ionic liquid as electrolyte, and $LiCoO_2$ as cathode. Focused ion beam (FIB) manipulation of a single nanowire enables the assembling of a prototype battery. Furthermore, due to the low vapor pressure of the ionic liquid, the whole system can be directly loaded into a TEM without sealing. The interface across the solid-ionic liquid was studied during charging and discharging using TEM imaging and electron energy loss-spectroscopy (EELS). By comparing these results with those obtained from batteries based on coin cell design, several challenges were identified. These results will be discussed along with the future research directions.

4:40pm **IS+AS-ThA9 Characterizing Solid Oxide Fuel Cells during Electrochemical Operation Using Ambient Pressure XPS**, ***F. El Gabaly***, *A.H. McDaniel,* Sandia National Laboratories*, M. Grass, Z. Liu, H. Bluhm, Z. Hussain,* Lawrence Berkeley National Laboratory*, G.S. Jackson, C. Zhang, S.C. Decaluwe,* University of Maryland, College Park*, K.F. McCarty, M.A. Linne, R.L. Farrow*, Sandia National Laboratories

Electrochemical systems for energy applications are hampered by lack of fundamental measurements and understanding of ion transport and interfacial charge transfer mechanisms. Electrochemical devices based on the conduction of O2- anions through a solid electrolyte, such as a solid oxide fuel cell (SOFC) or electrolyzer (SOEC), have great potential for both clean, efficient power generation and efficient production of fuels such as hydrogen or synthesis gas. The essential physical phenomena that govern reaction and charge transfer across material interfaces are poorly understood. The ability to directly observe changes in chemical composition and elemental oxidation state at surfaces and interfaces under electrochemically active conditions will provide insight into such processes. Here, we report in situ measurements of Ni and Pt patterned thin films (300nm) electrodes in solid-oxide electrochemical cells using ambient pressure X-ray photoelectron spectroscopy[1] (APXPS, Beamline 11.0.2 of the Advanced Light Source, Lawrence Berkeley National Laboratory). This novel setup provides quantitative information about the elemental surface composition, local surface potential in the yttria-stabilized zirconia electrolyte, and changes in elemental oxidation state as a result of electrochemical and thermochemical activity occurring under relevant operating conditions: typically 0.25 Torr of hydrogen and 0.25 Torr of water, T=1023K, and under applied bias potential. Chemical changes on the fuel cell electrodes under different electrochemical operation will be discussed, as well as the existence of transient species that could help reveal where and how the charge-transfer mechanism is occurring.

References

[1] D.F. Ogletree, H. Bluhm, G. Lebedev, C.S. Fadley, Z. Hussain, M. Salmeron, Rev. Sci. Instrum. 73 (2002) 3872.

This research was supported by the U. S. Department of Energy under Contract No.DE-AC04-94AL85000 (Sandia) and DE-AC02-05CH11231 (LBNL), and by Office of Naval Research under Contract No: N000140510711 (UMD) .

Magnetic Interfaces and Nanostructures
Room: C1 - Session MI+TF-ThA

Magnetic Thin Films: Multilayers and Nanostructures
Moderator: D.P. Pappas, National Institute of Technology

2:00pm **MI+TF-ThA1 Magnetic Recording Sensor Materials and Technology Above 1 Tb/in^2**, ***J.R. Childress***, Hitachi Global Storage Technologies **INVITED**

Magnetic recording is constantly evolving to reach specific technology targets. Today's hard disk drives can store information at >300 Gbit/in^2, and represent a striking example of nano-technology integrated into everyday life: data bits < 100nm x 20nm, read sensors with dimensions < 80nm, and read/write heads flying < 10nm above the disk. The specific challenge for the read sensor is to maintain adequate signal-to-noise ratio as its dimensions are reduced. For example, the development of recording head sensors for 1 Tb/in^2 and above requires sensors dimensions < 30nm. In this regime, all-metal current-perpendicular-to-the-plane (CPP) giant magnetoresistive (GMR) sensors are an attractive alternative to CPP tunnel-magnetoresistance (TMR) sensors. With typical resistance-area products in the range 0.03-0.10 Ω-μm^2, CPP-GMR sensors have the potential to deliver low sensor impedance at the smallest conceivable dimensions, and therefore lower noise and higher bandwidth performance. Among the challenges that CPP-GMR sensors face are low signal levels due to their low resistance, typically low DR/R when using thin magnetic layers, as well as current-induced noise and instability due to the spin-torque effect. I will review several paths that we have recently explored to increase signal and reduce spin-torque effects in CPP-GMR sensors. For increased signal, a key may be the synthesis and integration of new ferromagnetic thin-films alloys with high spin-polarization at the Fermi level (and therefore resulting in high magnetoresistance spin-valves), such as the predicted half-metallic Heusler alloys. For lower spin-torque effects we have demonstrated the effectiveness of dual spin-valves sensors, rare-earth cap layers for increased Gilbert damping, and synthetic-ferrimagnet free layers. I will present some of the physical concepts behind these approaches, and discuss recent data in the context of the specific technological requirements for magnetic recording around 1 Tb/in^2.

2:40pm **MI+TF-ThA3 Synthesis of Highly Magnetostrictive Single Crystal Fe$_{1-x}$Ga$_x$ Thin Films**, ***A. McClure***, *H Li,* Montana State University, *J.X. Cao, R.Q. Wu,* University of California, Irvine, *E. Arenholz,* Advanced Light Source*, Y.U. Idzerda*, Montana State University

The Fe$_{1-x}$Ga$_x$ alloy system is a highly anisotropic magnetostrictive material at the appropriate alloy concentration (termed Galfenol at x ~ 0.2) [1]. In thin film form, the atomic pinning of such a material to a substrate can strongly modify the magnetic anisotropy and therefore the magnetization dynamics in a non-isotropic manner, as is demonstrated by a strong angular dependence of the ferromagnetic resonance (FMR) linewidth.

Single crystal Fe$_{1-x}$Ga$_x$ thin films of various Ga concentrations were prepared on GaAs(001) and MgO(001) substrates by molecular beam epitaxy (MBE), with and without ZnSe buffer layers, respectively. For both substrates, reflection high energy electron diffraction (RHEED) measurements, performed *in-situ* during the growth, show single crystal epitaxial growth of the bcc structure for alloy compositions up to x = 0.7, well beyond the bulk stability region. Vibrating sample magnetometry (VSM) measurements show a reduction in the saturation magnetization with the incorporation of Ga, as well as a migration of the magnetic easy and hard axes that varies slightly between the two substrates. This slight variation is most likely due to the additional uniaxial magnetic anisotropy present in the films grown on the GaAs substrate due to the directional bonding from the zinc-blende surface. X-ray magnetic circular dichroism (XMCD) performed at the Fe L$_{2,3}$-edges reveals a very gradual decrease (10%) in the elemental Fe moment as the Ga concentration approaches 20% followed by a precipitous drop in moment for higher concentrations, while X-ray absorption spectroscopy (XAS) and XMCD measurements performed on the Ga L$_{2,3}$-edges show an evolution in the local Ga electronic structure (a narrowing of 1.6 eV in the L$_3$ peak position) and establishes an induced moment in the gallium of 0.1 m$_B$ anti-aligned to the Fe moment, in remarkably strong agreement with *ab-initio* density functional (GGA) calculations.

[1] A. E. Clark, J. B. Restorff, M. Wun-Fogle, T. A. Lograsso, and D. L. Schlagel, IEEE Trans. Magn. **36**, 3238 (2000).

3:00pm **MI+TF-ThA4 Anisotropic Transport in Manganite Films Driven by Selective Tailoring of Emergent Electronic Phase Separation**, ***T.Z. Ward***, *J.D. Budai, Z. Gai, J.Z. Tischler, L. Yin, J. Shen*, Oak Ridge National Laboratory

Complex oxides show a wide range of unique behaviors due to their often inseparable energy overlaps of spin-charge-lattice-orbital interactions. These interactions form the basis for emergent electronic phase separation in many complex materials which have been linked to exotic behaviors such as colossal magnetoresistance, the metal-insulator transition, and high T$_C$ superconductivity. By selectively tuning the energetic landscape that shapes the emergent formation of electronic phase separation, we have uncovered never before seen anisotropic transport properties that promise new tunable device applications while answering fundamental questions on the role of electronic phase separation in manganites. Using La$_{5/8-x}$Pr$_x$Ca$_{3/8}$MnO$_3$ (x = 0.3) (LPCMO) as a model system, we have found that we can selectively induce anisotropic electronic domain formation along one axis of a pseudocubic perovskite single crystal thin film manganite by epitaxially locking it to an orthorhombic substrate. Simultaneous temperature-dependent resistivity measurements along the two perpendicular in-plane axes show significant differences in the metal-insulator transition temperatures and extraordinarily high anisotropic resistivity on macroscales of up to 20000%. These findings show that emergent electronic phase domain formation can be selectively tuned over long distances which opens the door to new device engineering and a fuller understanding of the balanced energetics that drive emergent behaviors in complex materials.

3:40pm **MI+TF-ThA6 Spin-Torque Behavior of Perpendicular Anisotropy Nanopillar Devices**, ***E.E. Fullerton***, *I. Tudosa,* University of California, San Diego*, J. Cucchiara, S. Mangin,* U. Nancy, France*, Y. Henry,* IPCMS, France*, J. Katine,* Hitachi GST*, D. Ravelosona*, IEF, France **INVITED**

Spin torque reversal of nano-elements with perpendicular magnetic anisotropy have considerable interest for both the fundamental study of spin torque reversal and for possible spin-torque based devices. This ability to locally control magnetization opens the door to a range of applications such as high-density magnetic random access memories, tunable high frequency oscillators and possibly programmable logic devices. In perpendicular anisotropy systems the demagnetization field is commensurate with the anisotropy axis and can be described as an effective uniaxial anisotropy. Both the critical current for spin-torque reversal and the thermal stability are then proportional to the effective anisotropy [1-3] as shown experimentally for [Co/Pt]/[Co/Ni]/Cu/[Co/Ni] nano-pillar samples[2, 3]. In this presentation we describe recent experimental and theoretical studies of the influence of spin currents on the field and angular dependence of the free layer switching fields. The angular dependence of the switching field in the absence of current is well described by the Stoner-Wohlfarth asteroid for a uniaxial system. With the addition of current we find that spin-torque reversal is most efficient when the applied field is parallel to the anisotropy axis. Surprisingly, for fields applied at an angle to the anisotropy axis the switching fields are current independent for currents lower than a critical value and the critical current increases with increasing field angle. We will discuss the origin of this phenomena and results for coupled reversal of the free and reference layer.

[1]. J. A. Katine and E. E. Fullerton, J. Magn. Magn. Mater. **320**, 1217 (2008).

[2] S. Mangin et al., Nat. Mater. **5,** 210 (2006).

[3] S. Mangin et al., Appl. Phys. Lett. **94,** 012502 (2009).

4:20pm **MI+TF-ThA8 Spin Transfer Switching in Magnetic Tunnel Junctions with Co-Based Perpendicular Magnetic Anisotropy Multilayers***,* ***Z.R. Tadisina****, A. Natarajarathinam, S. Gupta, T. Mewes, P. LeClair,* University of Alabama*, E. Chen, S. Wang,* Grandis, Inc.*, W.F. Egelhoff*, NIST

Spin transfer switching (STS) has been studied for CoFeB/MgO/CoFeB magnetic tunnel junctions (MTJ) with perpendicular magnetic anisotropy (PMA) free and reference layers. The PMA multilayer material systems were studied as a function of bilayer thickness, bilayer ratio, and number of bilayers for Co/M multilayers, where M was Ni, Pd or Pt. After initial matrix experiments carried out to determine the experimental parameter space, a statistical Design of Experiments (DOE) was conducted to optimize the film structure that would maintain stable perpendicular anisotropy for a reasonable thickness of CoFeB, as well as minimize the damping parameter, α. For Co/Ni multilayers, the damping parameter varied from 0.016 to 0.023 as a function of the number of multilayers. As predicted and experimentally confirmed by others[1,2], we observed a critical thickness of Co above which the PMA disappears and in-plane anisotropy is observed. The magnetic behavior of these PMA systems was studied by vector magnetometry and alternating gradient magnetometry. X-ray diffraction, transmission electron microscopy (TEM) and local electrode atom probe (LEAP) studies were carried out to investigate the structure of the multilayers, interface smoothness, and growth of (111) texture as a function of deposition conditions and post-deposition annealing. Stress and magnetic force microscopy (MFM) studies confirmed the presence of stripe domains in the PMA stacks. The resistance-area (RA) product and tunneling magnetoresistance (TMR) of the unpatterned MTJ stacks were tested by current-in-plane tunneling (CIPT) measurements to optimize the MgO barrier and PMA stacks prior to actual device fabrication. The transport properties of the patterned MTJ stacks were tested in a PPMS system for both field and current switching from 10K to 400 K to test the thermal stability of these devices.

References:

1. O. Hellwig, A. Berger, J. B. Kortright, and E. E. Fullerton, “Domain structure and magnetization reversal of antiferromagnetically coupled perpendicular anisotropy films,” J. Magn. Magn. Mater., vol. 319, pp.13–55, May 2007.

2. M. Tekielak, P. Mazalski, A. Maziewski, R. Schäfer, J. McCord, B. Szyman´ski, M. Urbaniak, and F. Stobiecki, “Creation of Out-of-Plane Magnetization Ordering by Increasing theRepetitions Number N in (Co/Au)N Multilayers,” IEEE Trans. Magn. vol. 44, pp. 2850-2853, November 2008.

4:40pm **MI+TF-ThA9 Experimental Evidence for an Angular Dependent Transition of Magnetization Modes in Magnetic Nanotubes***,* ***O. Albrecht****, R. Zierold,* University of Hamburg, Germany*, C. Patzig,* Leibniz-Institute of Surface Modification, Germany*, S. Allende,* FCFM Universidad de Chile*, D. Görlitz,* University of Hamburg, Germany*, B. Rauschenbach,* Leibniz-Institute of Surface Modification, Germany*, K. Nielsch*, University of Hamburg, Germany

Highly anisotropic magnetic nanostructures maybe used to overcome the superparamagnetic limit found in magnetic nanoparticles. A well known approach which yields highly anisotropic structures is the creation of magnetic nanotubes. An established route for the fabrication of tubular structures is the use of porous alumina membranes as templates for subsequent covering with a magnetic layer by atomic layer deposition (ALD).

By using glancing angle deposition (GLAD), we present an new approach for a template synthesis to realize magnetic nanostructures.

The combination of GLAD and ALD techniques has the ability to build more complex magnetic nanostructures such as zigzag structures consisting of segmented tubes with adjustable angle between them.

We investigate the angular dependent magnetization determined by SQUID magnetometry at room temperature for all three directions in space.

The main result is the experimental evidence for theoretically predicted transition between two magnetization reversal modes (Vortex to Transverse).

5:00pm **MI+TF-ThA10 Experimental Observation of Ligand Induced Paramagnetism in CdSe Nanocrystals***,* ***J.R.I. Lee****,* Lawrence Livermore National Laboratory*, R.W. Meulenberg,* University of Maine*, S.K. McCall,* Lawrence Livermore National Laboratory*, K.M. Hanif,* Naval Research Laboratory*, J.C. Lang, D. Haskel,* Argonne National Laboratory*, L.J. Terminello, T. van Buuren*, Lawrence Livermore National Laboratory

The observation of magnetism has recently been reported for numerous nanoscale materials that do not demonstrate comparable behavior in bulk form. This is intriguing because coupling the magnetic properties of the nanocrystalline materials with their size-dependent optical and electronic behavior presents the potential for application in a variety of technologies. Identifying the origin of the magnetic properties is, therefore, of paramount importance. To date, several conflicting mechanisms have been proposed in studies of a number of nanoscale systems and, significantly, the cause of the magnetism remains a matter of some controversy in the literature. For example, the ferromagnetic behavior observed for Au nanocrystals (NCs) has been attributed to interactions with the organic surface passivant in one study and an intrinsic property of the nanoscale metal in another. Comparable sources have been also been proposed for the magnetic properties of CdSe NCs, along with an alternative possibility that defect sites are responsible. We report a systematic investigation of the effects of the surface passivant on CdSe NCs using a combination of x-ray magnetic circular dichroism (XMCD) spectroscopy, superconducting quantum interference device (SQUID) magnetometry and x-ray absorption spectroscopy (XAS). The suite of experiments demonstrates that, contrary to the findings of prior studies, our NCs are not ferromagnetic and instead exhibit paramagnetic behavior. In addition, the magnetic susceptibility is dependent on interactions with the organic molecule used to passivate the surface of the CdSe NCs. More specifically, the paramagnetic properties depend upon electron transfer at the molecular level via π-back donation between surface Cd atoms and the organic ligands.

Project 07-LW-041 was funded by the LDRD Program at LLNL. This work was partially supported by the OBES, DMR, under the auspices of the U.S. DOE by LLNL under Contract DE-AC52-07NA27344. Use of the ALS and APS was supported by the U.S. DOE, Office of Science, OBES, under Contracts DE-AC02-05CH11231 and DE-AC02-06CH11357, respectively.

5:20pm **MI+TF-ThA11 Artificial Nanomagnets With Lateral Confinement***, L. Yin,* **Z. Gai***, J. Shen, D. Xiao, Z.Y. Zhang,* Oak Ridge National Laboratory*, N. Widjaja,* The University of Tennessee, Knoxville*, E.W. Plummer*, Louisiana State University

We introduce a novel way—curved Cu(111) substrate—to smoothly modify the surface states by introducing a miscut angle and study the impact of modifying vicinal surface states on the ferromagnetic behavior of Fe nanodots. Fe nanodots are grown on a Cu(111)-curved substrate where the miscut angle changes from 0° (very large terrace width) to 8° (15-Å terrace width). With this curved substrate, the same growth parameter can be ensured in the whole miscut angle studied. When the Fe nanodot assemblies have an in-plane easy axis, two distinct regimes and a critical terrace width, separating these two regimes, can be identified. However, when the Fe nanodot assemblies have a perpendicular easy axis, we only observe one regime marked by a slight decrease in the critical temperature (T_c). There are three contributing factors: the vicinal surface state, the competition between the Fe nanodots diameter and the terrace width, and the in-plane uniaxial magnetic anisotropy. The couplings between these three factors lead to the interesting behavior observed in the Fe/vicinal Cu(111) nanodot assemblies. The vicinal surface strongly affects the coupling between Fe nanodots.

*Supported in part by Office of Basic Energy Sciences, U. S. DOE.

MEMS and NEMS
Room: B3 - Session MN+IJ+TR-ThA

Multi-scale Interactions of Materials and Fabrication at the Micro- and Nano-scale I
Moderator: A.V. Sumant, Argonne National Laboratory

2:00pm **MN+IJ+TR-ThA1 Silicon Carbide Thin Film Technology for Microsystems in Harsh Environments**, ***C. Carraro***, University of California, Berkeley **INVITED**

Whereas silicon has been the dominant semiconducting material for the fabrication of mechanical and electronic elements of micro-/nanosystems, its materials properties impose limitations on its use in harsh environment and demanding applications (e.g., repetitive contact, high temperature, high humidity). Silicon carbide thin film technology offers an alternative that enables such applications, thanks to its wider bandgap, higher melting/sublimation temperature, elastic modulus, fracture toughness, hardness, chemical inertness, and thermal conductivity. In this talk, I will review those SiC surface properties that are most different from silicon. I will then highlight recent materials, process, and characterization advances that are enabling SiC micro/nano systems for harsh environment and demanding applications.

2:40pm **MN+IJ+TR-ThA3 Sidewall Tribometer and Quartz Crystal Microbalance Study of a Self-Assembled Monolayer Lubricant Reservoir Effect**, ***D.A. Hook***, *B.P. Miller,* North Carolina State University, *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.[1] These and similar monolayers, however, have proven ineffective as MEMS lubricants alone. Indeed, even the most robust of SAM layers fails to protect devices from tribological failure for either normal or sliding cyclic contact [2]. Alternate schemes, such as vapor phase lubrication, must therefore be developed if progress is to occur. [3] The vapor phase of pentanol has recently been reported by Asay et al to extend the lifetime of a MEMS device in a mixture of dry nitrogen and various concentrations of pentanol. [4] This method of lubrication poses it's own set of issues in applications where devices need to be operated in native environments outside of lubricating vapors. Namely, does the vapor adsorb onto the surface in such a way that it will continue to lubricate in the native environment. In this study we have used a quartz crystal microbalance (QCM) to measure the adsorption and mobility of ethanol onto a surface coated with a perfluorodecyltrichlorosilane self assembled monolayer and a bare silicone surface. We have also used a MEMS sidewall tribometer to measure lifetimes of a SAM coated and uncoated device dosed with ethanol vapor. QCM measurements show that the self assembled monolayer retains ethanol on the surface once the vapor is removed and the tribometer lasts two orders of magnitude longer with the self assembled monolayer present once the ethanol vapor is removed. This data provides strong evidence that the self assembled monolayer acts as a lubricant reservoir and allows the residual ethanol to flow back into the contact area lubricating for extended periods of time.

Work funded by the AFOSR Extreme Friction MURI

1 Srinivasan, U., Houston, M.R., Howe, R.T., Maboudian, R., "Alkyltrichlorosilane-Based Self-assembled Monolayer Films for Stiction Reduction in Silicon Micromachines", Journal of Microelectromechanical Systems 1998, 7, 252-260

2 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, 104, 034303, (2008)

3 Krim, J., Abdelmaksoud, M., "Nanotribology of Vapor-Phase Lubricants" Tribology Issues and Opportunities in MEMS, B. Bhushan, ed. (Kluwer Academic, Dordrecht, 1998), pp. 273-284, invited

3:00pm **MN+IJ+TR-ThA4 *In situ* Reliability Studies of Interfacial Contact via a 2-axis MEMS Deflecting Cantilever Microinstrument**, ***F. Liu***, *I. Laboriante, C. Carraro, R. Maboudian*, University of California, Berkeley

Recent developments in the MEMS field have created a growing interest in the reliability of these miniaturized devices. Along with the reliability issues such as stiction, corrosion and friction, wear is an important failure mechanism in these microsystems. Repetitive contact between microelectromechanical systems (MEMS) surfaces can lead to device failure, making it highly desirable to develop a microfabricated instrument to study the effects of impact and wear in MEMS for a wide range of structural layers, contact mechanics, coatings, and ambients.

This paper describes the design, and testing of a microinstrument that allows the surfaces of two microstructures to come into contact, after which the surfaces are separated sufficiently in the substrate plane to allow nondestructive surface analysis and then, for the first time, re-engagement of the contact. The device is designed to achieve large enough in-plane deflection for *in situ* analysis and controllable contact load. Using this microinstrument, the time-dependent assessment of the contacting surfaces is achieved by scanning probe microscopy, including atomic force microscopy (AFM) and Kelvin probe force microscopy (KPFM), as well as scanning Auger electron microscopy (SAEM) and electrical contact resistance measurements. The microinstrument design also allows for the study of a wide range of materials, coatings and environmental conditions under controlled loads. The contact resistance initially decreases during the first tens of millions of impacts and then increase gradually, a behavior attributed to the wear. The fracture of Si grains shows up at around 24 billion impacts and grows to 5-6 grains in diameter after about 100 billion impacts, associated with the interfacial oxidation. Based on these results, potential wear mechanisms at the microscale are proposed.

4:20pm **MN+IJ+TR-ThA8 Traceable Determination of Cantilever Spring Constants with a MEMS-based Sensor**, ***T. Dziomba***, *S. Gao, U. Brand, K. Herrmann, L. Koenders*, Physikalisch-Technische Bundesanstalt (PTB), Germany

Apart from accurate determination of dimensional, i. e. geometric, features of small objects such as nanostructures and semiconductor structures, the quantitative determination of small forces in the range from µN (10^{-6} Newton) down to several ten pN (10^{-12} N) is essential for many research tasks. Applications range from force spectroscopy in nanobiotechnology to the determination of the mechanical properties of nanomaterials, biological structures and organic molecules. Most of these measurements are performed with scanning force microscopes (SFM) and cantilevers with integrated nanometric tips as probing elements. However the comparability of experimental results lack under the knowledge of cantilever stiffness and traceability of small forces.

With the help of special Metrology-SFMs as reference instruments at National Metrology Institutes (NMIs), a large variety of transfer standards as well as guidelines for characterization & dimensional calibration of SFM, the length traceability to the SI-unit meter has been successfully established for SFM in the past few years.

However, a similar traceability chain for the measurement of small forces still needs to be realized. NMIs face the challenge to expand the traceability chain down to small forces by developing special nanoforce primary standards. A further challenge is the development of transfer standards and/or measurement procedures which allow the user to conveniently calibrate cantilevers used for SFM and scanning force spectroscopy. Besides the deflection-calibration a simultaneous force-calibration of the cantilever is necessary.

The contribution describes the properties of a MEMS (Micro-Electro-Mechanical-System) comb drive actor which can be used as a force sensor. Traceable calibration of its stiffness is done using a nanoforce calibration device based on a high resolution compensation balance. The sensor used has a force resolution in the nN-range, a measurement range of up to 1 mN, a translation range of 8 µm and was used to quantitatively determine the stiffness of SFM cantilevers. Preliminary experiments demonstrate that the long-term stability of the sensor is better than 3.7×10^{-3} N/m (1 sigma) over 1 hour. After careful traceable calibration of its stiffness, the MEMS sensor has the capability to determine the stiffness of a great variety of cantilever types (from 100 N/m down to 0.1 N/m) with high accuracy. Thus a new micro-force and stiffness transfer standard with nN force resolution is available for the traceable stiffness calibration of SFM cantilevers.

4:40pm **MN+IJ+TR-ThA9 Improvement in Mechanical Contact Reliability with ALD TiO_2 Coating**, ***V. Pott***, *H. Kam, J. Jeon, T.-J. King Liu*, UC Berkeley

Introduction: In order to overcome energy limits of CMOS, micro-electro-mechanical relays are now being investigated. High endurance is required for relay-based ICs to be viable, and has been a challenge due to stiction and wear. In this work, we demonstrate that a mechanical contact can be made to be very reliable if the surfaces of the conductive electrodes are coated with an ultra-thin layer of titanium dioxide (TiO_2) by atomic layer deposition (ALD).

Device structure: A 3-terminal (3-T) relay design was used: an electrically conductive mechanical beam (source) is actuated electrostatically by applying a voltage to an underlying electrode (gate) separated from the beam by an air gap. If the applied bias is above a threshold voltage (V_{TH}), the tip of the beam is deflected to bring it into contact with a fixed electrode (drain).

Device fabrication: First, tungsten gate and source electrodes were formed on top of a thermally oxidized Si wafer using sputter deposition. Then, a sacrificial low-temperature oxide (LTO) layer was deposited and patterned. The top W electrode was then sputter deposited and etched. A heavily doped polycrystalline silicon-germanium (poly-SiGe) structural layer was then deposited and patterned. The top W electrode is attached to the bottom of the poly-SiGe beam. The beam was then released in HF vapor. Immediately afterwards, the relay was coated with ALD TiO_2 at 275°C using titanium tetrachloride ($TiCl_4$) as the precursor material. One ALD cycle consists of one pulse of $TiCl_4$ followed by Ti oxidation, and deposits ~0.25A of TiO_2. TiO_2 – W is a moderate potential barrier for electron in the ON state.

Results: W contacts were coated with either 3, 6 or 12 cycles of ALD TiO_2. 3 cycles coated contacts have poor stability and degrade with time. This is attributed to tungsten native oxide growth. Devices were characterized by applying an actuation bias V_{GS}=12V and source-drain bias V_{DS}=50mV. The estimated force in the contact region is 9μN. Measurements are done after 100 ON/OFF switching cycles, to stabilize the contact resistance. Linear I_{DS}-V_{DS} characteristics have been measured for both 6 and 12 cycles of ALD TiO_2. Reported contact resistances are 85.2kΩ and 1.47MΩ, for a contact area of $15\mu m^2$. No stiction or contact degradation is observed. If properly biased, 6 and 12 ALD TiO_2 cycles have an excellent yield and a good reliability (max. number of switching cycles tested thus far = 500).

Conclusion: We have found that coating of tungsten with ALD TiO_2 is an efficient way to reduce contacts ageing, stiction, and W oxidation. A contact resistance of 85.2kΩ has been measured and suggests the use of W-W contacts for relay-based ICs.

5:00pm **MN+IJ+TR-ThA10 Mass Producable, Multiple Stack, Integrated Micro Gas Chromatography System**, *K. Stacey, A. Knobloch, N. Chen,* GE Global Research, ***W.C. Tian***, National Taiwan University*, M. Shannon, R. Masel*, University of Illinois at Urbana-Champaign

This paper presents the novel wafer level processing, assembly, and characterizations of key components of a micro Gas Chromatography system (uGC). We demonstrated ways to perform wafer level low temperature bonding of silicon substrates and methods of patterning Metal Organic Frameworks (MOFs) within micropreconcentrators in a uGC. We also showed a polyimide membrane transfer process that is integral to the assembly of an electrostatic microvalve within our uGC. The overall device consists of multiple microvalves and a micropreconcentrator which are fabricated using a multiple wafer stack process and assembled using wafer level bonding. The entire process involves more than two hundred process steps including over tens of deep reactive ion silicon etching steps and multiple wafer bonds. We have succesfully fabricated functional preconcentrators and microvalves and have realized yields as high as 88%. In addition, full wafer microvalve assembly will improve device assembly time by 15-20x vs. die level assembly. The initial characterizations of micropreconcentrators and microvalves will be presented. In the future, the entire assembly of the system will be implemented.

Manufacturing Science and Technology
Room: C3 - Session MS-ThA

Manufacturing Issues in Nanoelectronics, PV and SSL
Moderator: C.Y. Sung, IBM Research Center

2:00pm **MS-ThA1 Nanoelectrical and Nanomechanical Interconnect and Device Metrology for CMOS Extension**, ***R.E. Geer***, *C.H. Chong, Y. Wang*, University at Albany **INVITED**

So-called ‘equivalent scaling’ which is dominating the extension of CMOS from the ‘pure’ scaling regime places inordinate demands on interconnect performance both for conventional CMOS switch configurations as well as alternate switch materials (III-V, carbon-based). As a result, substantial advances are required in fundamental metrology measurements of thin film electrical continuity in conventional intra-core and core-core interconnects as well as innovative approaches for electrical and mechanical interconnect metrology for alternate CMOS material sets. Here, we present nanoscale electrical continuity profiling of ultra-thin barrier and Cu films for conventional interconnects as well as nanoscale electrical metrology of alternate material (graphene-based) interconnects. For the former, it is shown that sub 2-nm films, although electrical conductive, show local reduction in electrical continuity that correlate to line-edge-roughness in patterned interconnect test structures. In contrast, alternate interconnect materials (e.g. single-layer graphene) are shown to exhibit electrical uniformity although local defectivity and electrostatic doping (for the case of interconnect applications) must be sufficiently controlled for use in conventional CMOS geometries.

2:40pm **MS-ThA3 New Mechanism for Optically Stimulated Point Defect Control In Ultra-Shallow Junction Formation**, *P. Gorai, Y. Kondratenko,* ***E.G. Seebauer***, University of Illinois at Urbana-Champaign

Formation of pn junctions in advanced Si-based transistors employs rapid thermal annealing (RTA) after ion-implantation in order to increase the activation of dopants. There has long been suspicion that the strong lamp illumination in RTA equipment may nonthermally influence the diffusion of dopants. The present work describes the evidence for a photostimulated diffusion mechanism based on electrostatic coupling between interface and Si bulk. Photostimulated effects on diffusion of boron were studied in ion implanted crystalline silicon samples. Low intensity illumination (2 W/cm^2) was used for nonthermal photostimulation during soak annealing using with resistive heating of the substrate. This experimental design allowed decoupling of heating and illumination. The samples were annealed at different temperatures and dopant diffusion and activation data was compared between experiments with and without illumination. Experimental data in conjunction with continuum simulations showed that light interacts with the charged defects at Si-SiO_2 interface and modulates the electrical field arising from near-surface band bending. The effects of this modulation exhibited profound effect on diffusion profile evolution near the surface and in the bulk. Simulations results were further employed to elucidate underlying physical mechanism of this effect.

3:00pm **MS-ThA4 Thickness/Composition Metrology of Ultra-thin Lanthanum Oxide Cap Layer for CMOS Metal Gate Work Function Tuning**, ***C.C. Wang***, *Y. Cao, G. Liu, X. Tang, Y. Uritsky, S. Gandikota*, Applied Materials Inc.

Beyond the 45 nm node CMOS application, metal gate and high-k dielectric are used and many new thin film materials are developed. In order to reduce the threshold voltage of the CMOS gate, the matching of the metal gate work function with the silicon band position is important. For NMOS work function tuning, lanthanum oxide (LaO_x) thin film is used. Device performance demands the use of less than 10 Å thick LaO_x and the stringent control of thickness and composition uniformity (1 to 2% 1σ) on 300 mm wafers. However, metrology of this new material is very difficult. First the LaO_x cap layer is so thin, only ellipsometry, X-ray photoelectron spectroscopy (XPS) and X-ray fluorescence spectroscopy (XRF) have the required sensitivity. Second, the composition of LaO_x changes with air exposure time due to its reaction with ambient moisture; such behavior renders ellipsometey and XPS ineffective, because the composition result and the thickness result from both techniques are strongly correlated in the case of ultra-thin film measurements. This leaves XRF to be the only candidate for both composition and thickness measurements. The main advantage of XRF is that the X-ray signals from the sample are proportional to the surface doses (atoms/cm^3) of the elements in the ultra-thin film; hence, it is simple to calibrate the tool and develop measurement recipes. To satisfy the new metrology needs, wavelength dispersive XRF (WD-XRF) and energy dispersive XRF (ED-XRF) techniques were developed.

For tool calibration and drift monitoring, a LaO_x thin film standard with known thickness, density and composition had to be prepared. Due to high reactivity of LaO_x in air, it was difficult to prepare a stable standard and to determine all its attributes. To overcome this problem, a 200 Å thick LaO_x thin film on silicon standard capped with a thin TiN layer was prepared, its thickness and density were measured by X-ray reflectivity and its composition was derived by the XRF measurement itself by an ingenuity method. Due to the good sensitivity of WD-XRF to both La and O signals, recipe was developed to monitor the composition of freshly deposited PVD LaO_x thin films and their change with ambient exposure time. The results showed that the LaO_x ultra-thin film deposited with lanthanum oxide target was more stable in air than those deposited with a La metal target. ED-XRF recipe was developed to monitor the LaOx thickness uniformity on 300 mm wafers. The main advantage of ED-XRF was its small X-ray spot size that afforded 3 mm edge exclusion measurements. Study showed ED-XRF had < 1% (1σ) precision with good throughput of < 60 seconds per data point.

3:40pm **MS-ThA6 Sidewall Image Transfer for Sub Lithographic Pitch Scaling for the 22nm CMOS Node & Beyond**, ***S. Kanakasabapathy***, IBM Research, *R.H. Kim*, Global Foundries, *A. Ko, A. Metz,* Tokyo Electron Limited, Japan, *T. Osabe*, Hitachi Technologies, Japan, *S. Schmitz, T. Standaert*, IBM Systems and Technology

Critical Dimension (CD) Scaling and Pitch Scaling for the past several decades have sustained the Microelectronics Industry’s march along the Moore ’s law. Wavelength, Numerical Aperture & Immersion assisted index scaling have made possible such pitch scaling in a fashion relatively transparent to Etch. However with the technical and manufacturing challenges faced by Extreme Ultraviolet (EUV) wavelength scaling, Etch/Integration assisted Pitch Scaling is being explored. Ground rule challenges have grown exponentially since Sidewall Image Transfer (SIT) was proposed as such a technique for pitch halving.

We present herein SIT challenges for obtaining sub 80 nm pitches for Line space levels compatible with Front End of Line applications. Line Edge Roughness (LER) and Line width Roughness (LWR) measurements for these integration schemes will be presented with options to mitigate them.

4:00pm **MS-ThA7 Wafer-level Process Sampling, Metrology and Testing for MEMS and Solar Photovoltaic Applications**, ***V. Ngo***, FEI Company

As MEMS (Micro-Electro-Mechanical Systems) devices further proliferate many industrial and consumer products, the need for fast characterization becomes critical to production process support and time-to-answer in failure analysis. For example, a Dual-Beam can be used to characterize the MEMS fabrication processes by cross-sectioning the area of interest using a focused ion beam and imaging the uncovered feature of interest for metrology and process evaluation using a scanning electron beam or via the ion beam itself. The ion-beam can also be used to weld and cross-section fragile suspended features without additional process steps such as resist backfilling. Most MEMS components, however, are very large on the order of 10s-100s microns, which can lead to long sample preparation times. Furthermore, localized gas chemistry injection on the micron-level at the point of beam-sample interaction further enhance milling rate to support wafer-level multi-site sampling for near-production process support. FA work in MEMS packaging and TSV development for MEMS-CMOS integration also have demonstrated benefits from the gas-enhanced FIB de-processing.

In addition to sample preparation throughput, it is possible to use a micromanipulator probe to remove specific components of the device for characterization. This work also demonstrates that A FIB system configured with such an in-situ sample lift-out probe can remove specific components at their attachment points and lifting them out to characterize their etch profile, rather than attempting to ion mill a large area away to enable access. Both gas-enhanced and lift-out approaches can significantly reduce the amount of time required for a cross-section of the device, and improve the quality of data obtained.

4:20pm **MS-ThA8 Establish Degradation Rates of Photovoltaic Modules and Systems Trough Comprehensive Electrical and Mechanical Analysis**, ***A. Leyte-Vidal***, *K. Davis, W. Wilson, R. Reedy, N. Hickman,* Florida Solar Energy Center, *S. Kurtz*, National Renewable Energy Laboratory

Performance degradation of photovoltaic modules and systems follows a progression that is dependent on multiple factors. Many of the mechanisms responsible for degradation are difficult to simulate in a laboratory setting. While accelerated aging tests are a valuable tool in evaluating photovoltaic components and systems, long-term monitoring of systems installed in the field is the true test of reliability. A comparison of the original and weathered power output of several different photovoltaic technologies dating back to 1998 is presented here, along with an analytical description of the degradation and weathering effects responsible for reduced power production over extended periods of time. Experimental data has been collected on diverse generations of photovoltaic modules installed throughout the state of Florida, where the systems have been subjected to long-term exposure in a hot, humid climate. Some of the module degradation mechanisms may be attributed to optoelectronic effects, while others are more mechanical in nature (e.g. encapsulation and delamination issues). The effect of performance degradation on the system's economics and life-cycle energy costs has been presented in order to better quantify the impact of the different degradation mechanisms. While working to reduce the initial degradation effects is of vital importance and has received considerable interest in the past, a better understanding of the long-term degradation mechanisms inherent in this technology is also fundamental in the effort to improve the reliability of photovoltaic modules and systems.

Nanometer-scale Science and Technology
Room: L - Session NS-ThA

Characterization & Imaging at the Nanoscale II
Moderator: U. Schwartz, Yale University

2:00pm **NS-ThA1 Nanoelectrical Probing with Multiprobe SPM Systems Compatible with Scanning Electron Microscopes**, *J. Ernstoff,* Nanonics Imaging Ltd., Israel, ***A. Lewis***, Hebrew University of Jerusalem, Israel, *A. Ignatov, H. Taha, O. Zhinoviev, A. Komissar, S. Krol, D. Lewis*, Nanonics Imaging Ltd., Israel

A scanning electron microscope compatible platform that permits multiprobe atomic force microscopy based nanoelectrical characterization will be described. To achieve such multiple parameter nanocharacterization with scanning electron microscope compatibility involves a number of innovations both in instrument and probe design. This presentation will focus on how these advances were achieved and the results obtained with such instrumentation on electrical nano-characterization and electrical nano-manipulation. The advances include: 1. Specialized scanners; 2. An ultrasensitive feedback mechanism based on tuning forks with no optical feedback interference that can induce carriers in semiconductor devices; and 3. Unique probes compatible with multiprobe geometries in which the probe tips can be brought into physical contact with one another. Experiments will be described with such systems that will include multiprobe electrical measurements with metal and glass coated coaxial nanowires of platinum. This combination of scanning electron microscopes integrated with multiprobe instrumentation allows for important applications not available today in the field of semiconductor processing technology.

2:20pm **NS-ThA2 Nanocone Chemical Analysis with High Resolution Scanning Auger Microscopy**, ***S.N. Raman***, *J.S. Hammond, D.F. Paul, D.G. Watson, P.E. Larson, R.E. Negri*, Physical Electronics

The recent dramatic increase in nanotechnology research has pushed the development of analytical techniques to elucidate the growth mechanisms of nanostructures. Scanning electron beam techniques, including Scanning Auger Microscopy, have provided valuable imaging and elemental characterization tools for these structures with a spatial resolution better than 10 nm. To enhance the Auger analysis for nanocones, high energy resolution chemical state spectroscopy and imaging has been combined with the imaging capabilities of a CMA based Scanning Auger. Using a combination of these Auger analytical capabilities, the analysis of nanocones grown by plasma enhanced chemical vapor deposition reveals a non-uniform chemical composition between several different nanocones. The quantitative elemental analysis as well as the imaging of different chemical states has been obtained without imaging artifacts induced by the shapes of the vertically oriented nanocone structures. These results provide further insights into the nanocone growth mechanisms.

2:40pm **NS-ThA3 Epitaxial Growth of Al on Sapphire for Qubit Applications**, ***F. da Silva***, University of Colorado, Denver, *B.P. Gorman, M. Kaufman,* Colorado School of Mines, *J.S. Kline, D.A. Braje, D.S. Wisbey, D.P. Pappas*, National Institute of Standards and Technology

The pursuit of new low loss materials and epitaxial structures to enhance the performance of superconducting quantum bits (qubits) has heightened in recent years. The small number of defects observed in epitaxially grown structures, compared with polycrystalline and amorphous materials, accounts for several improvements reported in qubit operation such as the reduction in the density of two-level fluctuators and longer coherence times **[1]**. Qubit structures of interest are superconductor-insulator-superconductor (SIS) tri-layers deposited on an insulating substrate. Two candidates for the substrate and superconductor metal are sapphire (α-Al_2O_3) and Al respectively **[2]**. Complete defect removal requires a study of each layer and its corresponding interfaces. In this work we focus our attention on the interface between the substrate and the first superconductor layer. We used transmission electron microscopy (TEM) techniques to analyze the growth of Al (111) films on sapphire (0001) substrates. While the sapphire substrate induces the growth of epitaxial Al along a <111> direction as desired, the subsequent [111[planes grow with either ABC or ACB stacking resulting in twin-related "grains" within the epitaxial film. In addition, slight (1-5°) in-plane misorientations are observed in adjacent, twin-related Al grains and appear to correspond to the slight rotations between the oxygen atoms along the c-axis of the sapphire. In other words, because the Al orients itself with the oxygen atoms on the sapphire basal planes, any miscuts of the sapphire substrate to within ±1/6 of the unit cell c-axis will slightly misorient the Al due to the slight rotation of the oxygen atoms with respect to the c-axis of the sapphire cell **[3]**. Finally, these twinning and misorientation effects appear to induce other growth defects in the subsequent layers used in the qubit circuit. Based on these results, we propose the use of a chemically compatible oxide buffer layer which does not have rotations between successive O layers within its unit cell.

[1] S. Oh, K. Cicak, J. S. Kline, M.A. Sillanpää, K.D. Osborn, J.D. Whittaker, R.W. Simmonds, and D.P. Pappas, Phys. Rev. B **74**, 100502R (2006).

[2] J. Martinis, Quantum Information Process **8**, 81 (2009).

[3] D.L. Medlin, K.F. McCarty, R.Q. Hwang, S.E. Guthrie, and M.I. Baskes, Thin Solid Films **299**, 110 (1997).

3:00pm **NS-ThA4 Real Time Scatterometry for Profile Control during Resist Trimming Process in a HBr/O_2 Plasma**, ***M. El Kodadi***, LTM-CNRS, France, *S. Soulan, P. Schiavone,* Georgia Institute of Technology, *M. Besacier*, LTM-CNRS, France

In situ , real time control of the different process steps in semiconductor device manufacturing becomes a very important challenge, especially for the lithography and plasma etching processes. We have developed a specific software and hardware tools to perform dynamic scatterometry, using in situ spectroscopic multi-wavelength ellipsometry. This technique is non-invasive, non-destructive optical metrology technique. It uses the analysis of the signature of the light scattered by periodic structure to infer the shape of a feature.

In this study the authors show that dynamic scatterometry can be used for real time monitoring during the resist trimming process of two different resist materials, the M78Y resist from JSR, exposed at 248nm wavelength using an ASML/300 scanner, and the 193 nm resist "JSR 1682" . The etch gases used in this study are HBr and O_2.with two different bias power conditions "0 and 50" WBias power. Then we discuss about the influence of chemistries and bias power on the etched profile. We report how the plasma conditions can induce some chemical modifications of the resist films, and we explain how this issue can be addressed in the scatterometric real time control of the resist trimming process. A Jobin-Yvon ellipsometer, capable of real time acquisition of sixteen wavelengths, is plugged onto chamber of a Decoupled Plasma Source (DPS) from Applied Materials. The measurements are made in real time in the etch chamber during the process.

For validation purposes, the same process has been interrupted at several different times and the trimmed feature profiles have been measured using a 3D AFM from Veeco Instruments. The comparison between scatterometry and AFM measurement shows an excellent match for both CD and height parameters with a difference less than 2% .

This proves that dynamic scatterometry provides reliable results and shows a great potential as a real time monitoring technique for etch process control. This characterization technique can be viewed as an invaluable tool for the accurate control of the patterning of current and next generations of semiconductor devices.

3:40pm **NS-ThA6 Advancing QPlus AFM Performance at 5K Towards Lower Oscillation Amplitudes and Higher Frequencies**, *A. Bettac, J. Koeble,* ***K. Winkler***, *B. Uder, M. Maier, A. Felz*, Omicron NanoTechnology GmbH, Germany

The QPlus sensor with its high spring constant and an optimized quality factor allows operation at very small oscillation amplitudes and is therefore ideal for atomically resolved imaging on all types of surfaces, i.e. for insulators, semiconductors and also for metallic surfaces. We have integrated the QPlus technology into an established low temperature STM platform. The extremely low signal of the QPlus sensor due to small oscillation amplitudes requires the first amplification stage to be very close to the sensor, i.e. it has to be compatible with low temperatures.

We present atomic resolution imaging on single crystal NaCl(100) with oscillation amplitudes below 100 pm_{pp} (peak to peak) and operation at higher flexural modes at frequencies of up to 318 kHz in constant df imaging feedback at 5K. We also present atomic resolution measurements on metallic Au(111) and Ag(111) surfaces with an extremely high stability at 5 K [1]. On a reconstructed Si(111) 7x7 surface further investigations in a temperature range between 50 K and 1070 K demonstrate the capability of the QPlus sensor for ultimate resolution in pure NC-AFM and dynamic STM measurements. At low temperatures, atomically resolved images of the rest atom layer will be presented. High temperature measurements close to the phase transition between the (1x1) and (7x7) show dynamics in the formation of step edges and kinks.

[1] A. Bettac, J. Koeble, K. Winkler, B. Uder, M. Maier, and A. Feltz, Nanotechnology, in print

4:00pm **NS-ThA7 Monatomic In Adatom Chains Assembled on the InAs(111)A Surface by Low-Temperature Scanning Tunneling Microscopy**, ***J. Yang***, Paul Drude Institute for Solid State Electronics, Germany, *K. Kanisawa,* NTT Corporation, Japan, *Ch. Nacci, S. Fölsch*, Paul Drude Institute for Solid State Electronics, Germany

Atom manipulation by scanning tunneling microscopy (STM) at cryogenic temperatures has proven to be a powerful experimental tool to study the physics of assembled nanostructures at surfaces. Since its implementation in the early 1990s [1], STM-based manipulation has been applied mainly to atoms and molecules adsorbed on metal surfaces. Here we demonstrate the extension of this technique to III-V semiconductor materials and report the fully reversible repositioning of In adatoms on a InAs (111)A surface by vertical manipulation at 5 K, i.e., by transferring individual atoms from the surface to the STM tip and vice versa. This allows us to assemble compact structures with the In atoms added one by one and occupying nearest-neighbor vacancy sites of the (2x2)-reconstructed surface (separation of the vacancy sites $a_0\sqrt{2}$=8.57 Å, a_0: cubic InAs lattice constant). Combining this approach with scanning tunneling spectroscopy (STS), we studied the electronic properties of monatomic adatom chains representing a model case of a one-dimensional electron system. The STS data reveal substantial electronic coupling between the In chain atoms leading to the formation of an unoccupied quantum state delocalized along the chain. Regarding the substantial interatomic spacing of 8.57 Å present here it appears that substrate-mediated coupling is essential for the along-chain linking rather than direct interatomic coupling reported previously in metal-on-metal adatom chains [2,3]. Our results demonstrate that the combined approach of atom manipulation and local spectroscopy is applicable to explore atomic-scale quantum structures in a semiconductor-based system.

[1] J. A. Stroscio and D. M. Eigler, Science 254, 1319 (1991).

[2] N. Nilius, T. M. Wallis, and W. Ho, Science 297, 1853 (2002).

[3] S. Fölsch, P. Hyldgaard, R. Koch, and K. H. Ploog, Phys. Rev. Lett. 92, 56803 (2004).

Support by the Japanese Agency of Science &Technology (JST) and the German Research Foundation (DFG) is gratefully acknowledged.

4:20pm **NS-ThA8 Making Mn Substitutional Impurities in InAs using a Scanning Tunneling Microscope**, ***Y.J. Song***, NIST and University of Maryland, College Park, *S.C. Erwin,* Naval Research Laboratory, *G.M. Rutter,* National Institute of Standards and Technology, *P.N. First,* Georgia Institute of Technology, *N.B. Zhitenev,* National Institute of Standards and Technology, *Y. Kuk,* NIST and Seoul National University, Korea, *J.A. Stroscio*, National Institute of Standards and Technology

The ability to manipulate single atoms has been demonstrated for both lateral and vertical manipulation using a tunable chemical-bond interaction between the scanning tunneling microscope (STM) probe tip and adsorbed atom [1]. More recently a new form of atom manipulation involving the exchange of two different surface atoms has been observed with Mn atoms on III-V surfaces; the motivation being the understanding magnetic interactions in these dilute magnetic semiconductors [2]. In this presentation we discuss detailed measurements and theoretical calculations of the STM induced exchange of Mn and In atoms on the InAs(110) surface. Mn was deposited onto the InAs(110) surface at 7K and were observed as single adatoms. We used the STM to artificially substitute the single Mn adatoms with In atoms in the top-most surface layer. This process involves raising the sample tunneling voltage beyond a certain threshold voltage of approximately -0.6 eV. We determined the statistical analysis of the threshold voltages for different offset tunneling currents and measured high resolution STM images of the initial and final Mn states as a function of tunneling voltage. We calculated the pathway and energetics for this atomic exchange with density functional calculations and compare with the STM measurements.

[1] J. A. Stroscio and D. M. Eigler, Science **254**, 1319 (1991).

[2] Dale Kitchen *et al*, Nature **442**, 436 (2006).

Plasma Science and Technology
Room: A1 - Session PS1-ThA

Fundamentals of Plasma-Surface Interactions II
Moderator: D.J. Economou, University of Houston

2:00pm **PS1-ThA1 Negative Ion Surface Production in Low Pressure Plasma**, ***G. Cartry***, *L. Schiesko, J.M. Layet, M. Carrere*, PIIM, Aix - Marseille Université - CNRS, France **INVITED**

Negative ions in plasmas play a main role in the discharge kinetics. For instance they may be at the origin of plasma instability [1], or may be responsible for coalescence in the primary state of dust formation [2]. Plasma based negative ion sources can have many applications. They may be used to reduce surface charge during plasma etching and in the context of controlled fusion research, they are used to generate neutral beams to heat fusion plasma. Therefore controlling negative ion production and loss in plasmas is of primary interest in many research fields. Efficient negative ion sources use caesium deposited on surfaces to increase negative ion production. Indeed, due to its property of reducing the work function, caesium leads to a high negative ion surface production yield. Negative ions are also produced in plasma bulk through electron attachment on molecules. Up to now most of works focused on plasma bulk production and on caesiated-surface production. Few works deal with caesium free surface production while almost all low pressure plasma sources are running without caesium. The aim of the present paper is to study caesium free negative ion surface production in low pressure plasmas.

Our first study is concerned with H2/D2 plasmas and graphite material for fusion applications [3]. However, results obtained here can be extended to low pressure plasma sources used in microelectronic industry for instance, since carbon containing materials are often in interaction with H2 plasmas or even more electronegative plasmas such as oxygen, fluorine or chlorine containing plasmas.

We use a helicon reactor whether in capacitive or inductive mode. A mass spectrometer is placed in the diffusion chamber of the helicon reactor and faces a one square centimetre graphite sample. The sample is negatively biased with respect to the plasma. Positive ions (H+, H2+, H3+) bombards it and negative ions formed (H-) upon bombardment are repelled from the surface toward the plasma. Under low pressure considered here, they reach without any collision the mass spectrometer where they are analysed according to their energy. Study of negatve Ion Distribution Function (IDF) provides information on surface production mechanisms. In this talk we will discuss IDFs measurements, describe how we identify surface production mechanisms, show negative ion surface production yield dependency with positive ion flux and energy, and compare H2 and D2 plasmas.

The authors acknowledge ANR (project ITER-NIS BLAN08-2_310122)

[1] Chabert P et al 2001 Pl. S. Sci. Tech.10 478

[2] Bouchoule A et al 1996 Pure Appl. Chem.68 1121

[3] L Schiesko et al Pl. S. Sci. Tech.17 (2008) 035023

2:40pm **PS1-ThA3 Amorphous Hydrogenated Carbon Etching with a Low Energetic Plasma Jet**, ***T.A.R. Hansen***, *J.W. Weber, M.C.M. van de Sanden, R. Engeln*, Eindhoven University of Technology, The Netherlands

Structures in the chip industry are approaching the 32 nm half pitch, which requires radiation in the VUV and EUV range. Cracking of hydrocarbon impurities in the vacuum by the radiation causes C growth on the VUV and EUV optics. Each nm of deposited carbon reduces the reflectivity of the optics by 1%. Fast removal of these contamination layers without damage to the underlying optics is essential for the next generation of lithography devices.

Etching with a low energetic plasma jet can be used to selectively remove coatings such as hydrogenated amorphous carbon (*a*-C:H) without damage to the underlying structure. Real time, *in situ* spectroscopic ellipsometry measurements indicate that the highest etch rates are obtained for an Ar/H$_2$ plasma, rather than for a pure Ar or H$_2$ plasma.

Even though the etch rate of *a*-C:H thin films is dependent on both temperature and roughness, the highest roughness in absolute values is attained by the plasma with the lowest etch rate. At low temperatures, the etch rate deviates from an Arrhenius relation, while the activation energy is similar for both the H$_2$ and Ar/H$_2$ plasma at higher temperatures.

The two orders of magnitude higher etch rate for the Ar/H$_2$ plasma is due to chemical sputtering, which is a synergistic effect between atomic H and Ar$^+$ ions with an ion energy below the threshold of 58 eV for physical sputtering. Chemical sputtering has been observed by Hopf et al. for energies above 20 eV and an H to Ar$^+$ flux ratio over 100 [1]. In our plasma, however, the Ar$^+$ ion energy is only a few eV's and the estimated H to Ar$^+$ ratio is lower than 5.

The etch products, released from the surface, consist mainly of CH$_4$ and C$_2$H$_y$, as shown by residual gas analysis. Time resolved optical emission spectra of the Ar/H$_2$ plasma, from a few mm's in front of an *a*-C:H sample, indicates also the presence of C$_2$ and CH radicals. The CH radical is formed in the plasma phase through charge transfer between Ar$^+$ ions and these larger hydrocarbons, and dissociative recombination. Similar plasma chemical processes occur during the remote plasma deposition of *a*-C:H films. However, in contrast with deposition, the CH rotational temperature shows an overpopulation in the higher excited states, indicating that the (internal state of the) parent molecule is different for an etch plasma than for a deposition plasma. Spatially resolved optical emission measurements are Abel inverted, by means of the numerical Barr method. While there is some CH production throughout the entire plasma jet, the highest CH production occurs in front of the *a*-C:H sample.

[1] C. Hopf, A. von Keudell and W. Jacob, Nucl. Fusion **42** (2002) L27–L30

3:00pm **PS1-ThA4 Investigation of Fluorocarbon PECVD During Processing of Si and ZrO$_2$ Surfaces**, ***M. Cuddy***, *E.R. Fisher*, Colorado State University

Films deposited from fluorocarbon (FC) plasmas exhibit low dielectric constants desirable for interlayers in ultra-large scale integrated circuits (ULSIs). The processing of ULSIs has involved the use of small monomer (CF$_4$, C$_2$F$_6$) FC precursors as an avenue for plasma-enhanced chemical vapor deposition (PECVD). To gain a broader understanding of both the FC plasma system and plasma-surface interactions, we have explored gas phase diagnostics and species-surface reactivity under varying plasma parameters. This presentation will reflect upon data obtained from optical emission spectroscopy (OES) concerning the role of excited state species present in FC plasmas. OES data show that during FC plasma treatment of Si and ZrO$_2$ wafers, CF$_2$* concentrations increase independent of feed gas and substrate type. The films deposited from such treatments do, indeed, consist of FC moieties and thus plasma-surface interactions are clearly influential in the overall process. We have studied the interaction of FC plasma species at the interface of depositing films using the imaging of radicals interacting with surfaces (IRIS) technique. IRIS data show that scatter probabilities for the CF$_2$ radical are greater than unity, indicating that CF$_2$ is produced from films *at the surface* during FC plasma processing of silicon. Furthermore, we have used quadrupole mass spectrometry to investigate mean ion energies of CF$_2^+$ in FC plasmas and have discovered that ion energies increase with increasing applied rf power. We have previously demonstrated that IRIS scatter coefficients for CF$_2$ produced from larger precursors (C$_3$F$_8$ and C$_4$F$_8$) correlate directly with ion energy. Thus, we will explore the role of this radical during processing of Si and ZrO$_2$ with small FC precursors as monitored by IRIS studies and compare these results with the respective ion energies for CF$_2^+$ in these systems.

3:40pm **PS1-ThA6 Studies of Chlorine-Oxygen Plasmas and Evidence for Heterogeneous Formation of ClO and ClO$_2$**, ***V.M. Donnelly***, *J. Guha*, University of Houston

Plasma and surface diagnostics of Cl$_2$/O$_2$ mixed-gas inductively coupled plasmas are reported. Using trace rare gas optical emission spectroscopy (TRG-OES) and Langmuir probe analysis, electron temperatures (T$_e$) and number densities for Cl atoms (n$_{Cl}$), electrons (n$_e$), and positive ions were measured as a function of percent O$_2$ in the feed gas and position in the plasma chamber. Adsorbates on, and products desorbing from a rotating anodized aluminum substrate exposed to the plasma were detected with an Auger electron spectrometer and a quadrupole mass spectrometer. T$_e$ and n$_e$ increased with increasing percent O$_2$ in the plasma, while n$_{Cl}$ fell off with O$_2$ addition in a manner reflecting simple dilution. Cl atom recombination probabilities (γ_{Cl}) were measured and were found to be a nearly constant 0.036±0.007 over the range of Cl$_2$/O$_2$ mixing ratios and Cl coverage. Large yields of ClO and ClO$_2$ were found to desorb from the surface during exposure to the plasma, ascribed predominantly to Langmuir-Hinshelwood reactions between adsorbed O and Cl. In addition, the transient surface composition of an anodized aluminum surface was determined as the gas was switched from Cl$_2$ to O$_2$ and vice versa. When the surface was first conditioned in an O$_2$ plasma and then exposed to Cl$_2$ plasmas, a rapid uptake of Cl was found in the first tens of seconds, followed by a slow approach to a steady state value within ~5 minutes of plasma exposure. Conversely, when the surface was exposed to a Cl$_2$ plasma for a long time and then switched to an O$_2$ plasma, the anodized aluminum surface underwent a rapid de-chlorination in the first few seconds and then a slow approach to steady state over ~3 minutes. The buildup and decay of Cl coverage is well described by a stretched exponential function, reflecting a range of binding sites for Cl. Throughout these treatments, the coverages of Si (from erosion of the quartz discharge tube) and O was nearly constant.

4:00pm **PS1-ThA7 Etching of Silicon and Silicon Oxide in a Pulsed Inductively Coupled Plasma with Chlorine**, ***C. Petit-Etienne***, LTM/UJF, France, *L. Vallier, E. Pargon, O. Joubert*, LTM/CNRS, France

For the next technological generations of integrated circuits, the traditional challenges faced by etch plasmas (profile control, selectivity, critical dimensions, uniformity, defects, ...) become more and more difficult, intensified by the use of new materials, the limitations of lithography, and the recent introduction of new device structures and integration schemes. Chemical plasma composition can be changed by modifying the gas mixture, ion flux can be partly controlled by source power, and ion energy can be chosen thanks to the bias voltage applied to the substrate. However, these control parameters are not always sufficient to reach all required etching characteristics and new control parameters are needed. Pulsing the plasma source power or the substrate bias offers new operating parameters (pulse frequency, duty cycle). The main advantages of a pulsed etching process are the improvement of etch selectivity and the reduction of charge-up damages and defects by reducing the electron activity and controlling the dissociation of radicals in the plasma.

Studies are being conducted on the etching characteristics of silicon and silicon dioxide in a 300 mm industrial inductively coupled plasma etching chamber having pulsed plasma discharge capability from Applied Materials. The reactor has been modified to be connected to an Angle-Resolved X Ray Photoelectron spectroscopy analyzer by a robotized vacuum chamber. Hence after an etching process, XPS spectra were recorded as function of take-off angle and the integrated intensities of the core-level peaks were used to obtain chlorine concentration and chemical state information from different depths of the sample, thereby permitting non-destructive characterization of chlorine profile in thin silicon oxide films. Material etch rates were measured in real time by in situ multi-wavelength ellipsometry.

When the plasma is pulsed, two parameters can be adjusted, namely the frequency of the pulse and the duty cycle. While the frequency has only a small influence on the etch rates in the investigated frequency range, our results demonstrate that a low duty cycle clearly modifies etch rate and can considerably improve the etch selectivity between silicon and silicon oxide. When a thin silicon gate oxide layer is exposed to very low energy etching conditions, a first step of chlorine incorporation is observed before etching. Preferential accumulation near the SiO_2/Si interface is observed and chlorine is shown to bond to both silicon and oxygen in multiple distinct chemical states.

4:20pm **PS1-ThA8 Fully Atomistic Profile Evolution Simulation of Nanometer-scale Si Trench Etching by Energetic F, Cl, and Br Beams**, ***H. Tsuda***, *T. Nagaoka, K. Eriguchi, K. Ono,* Kyoto University, Japan*, H. Ohta*, University of California, Santa Barbara

An atomic-scale understanding of interactions between chemically reactive plasmas and surfaces is required to establish nanometer-scale processing technologies. Various numerical studies based on molecular dynamics (MD) simulation have been reported so far, but these were limited to simulations of the simple blanket etching to estimate microscopic etching properties [1,2]. Here, we first report a fully atomistic silicon feature profile simulation using classical MD simulations. The potential form can be found in our previous papers [2,3,4]. F, Cl, and Br beams with a translational energy of 100 eV were used as reactive species. The surface area of Si (100) substrates was about 163 × 22 $Å^2$, where 3840 silicon atoms were initially located in the structure of diamond lattice. M ask patterns were introduced in the direction parallel to the short axis with periodic condition, in order to reproduce the trench etching feature. Then, the area without mask was 50 × 22 $Å^2$. By using our new atomistic profile evolution simulation, we investigated halogen plasma-surface interactions at sidewalls and bottom surfaces of nanometer-scale Si trench in detail. It was found that specific feature profiles with different gaseous species appear not only at the sub-micrometer-scale but also at the nanometer-scale etching, and the difference of surface reaction layer formation strongly affects the feature profile evolution during etching. For instance, fluorine beam etching showed that fluoride layer is formed on the entire surfaces containing sidewalls and bottom surfaces, thus giving isotropic etching. Chloride layer was thicker than fluoride and bromide layers, to give feature profiles of sidewall tapering. Bromide layer on bottom surfaces was thinnest among the three, and so the etching rate was lowest. So, it was cleared that the surface reaction layer formation strongly affects the feature profile evolution during etching. Our approach is essential as a reference for macroscopic or empirical profile simulation, where simulation sizes have been reduced recently. We also show some comparison between MD-based profile simulation and our empirical profile simulation (atomic-scale cellular model [5]).

[1] H. Ohta *et al*., J. Vac. Sci. Technol. A **19**, 2373 (2001).

[2] T. Nagaoka *et al*., J. Appl. Phys. **105**, 023302 (2009).

[3] H. Ohta and S. Hamaguchi, J. Chem. Phys. **115**, 6679 (2001).

[4] H. Ohta *et al*., J. Appl. Phys. **48**, 020225 (2009).

[5] Y. Osano and K. Ono, J. Vac. Sci. Technol. B **26**, 1425 (2008).

4:40pm **PS1-ThA9 Molecular Dynamics Simulations of Oxygen-Containing Polymer Sputtering and the Ohnishi Parameter**, ***G.K. Choudhary****, J.J. Végh, D.B. Graves*, University of California, Berkeley

The effects of ion bombardment on polymer surfaces can be profound, with implications for all plasma-based pattern transfer processes that involve the use of polymer etch masks in lithography and etching. It is known that Ar^+ bombardment of various polymers results in the formation of a 1-2 nm deep cross-linked region at the exposed surface, and that virgin polymer sputtering yields can be several orders of magnitude higher than steady state yields after ion bombardment. [1]

In this talk, we report results from molecular dynamics (MD) simulations of Ar+ (~ 40 - 150 eV) sputtering of oxygen-containing polymers. The MD data are compared to available experimental results, with special focus on the so-called Ohnishi parameter, which has been shown to correlate with sputtering yields for many O-containing polymers. [2] The MD simulations match the published correlations well, and we present a quantitative model of sputtering for these polymers that shows why the Ohnishi parameter (a function of the polymer composition) is proportional to the steady state sputtering yield.

However, we also show that the Ohnishi parameter does not correlate with yields for other polymers, including polyfluoroethylene and polyethylene. The MD simulations show that the validity of this parameterization is dependent on whether or not the sputtering of the polymer transitions between ion-induced scissioning to cross-linking at steady-state.

Finally, we discuss the implications of the dynamics of ion-induced surface cross-linking for synergistic photoresist roughening that occurs in plasmas, especially in the presence of vacuum ultraviolet photon and/or beaming electron exposure.

[1] J. J. *Végh, D. Nest, D. B. Graves et al. " Near-surface modification of polystyrene by Ar+: molecular dynamics simulations and experimental validation" Applied Physics Letter, vol. 91, pp. 233113-1-3, 2007.*

[2] H. Gokan, S. Esho, and Y. Ohnishi, "Dry etch resistance of organic materials," J. EZectrochem. SOC., vol. 130, pp. 143-146, 1983.

5:00pm **PS1-ThA10 Charge Trapping and Valence-band Structure of VUV-Irradiated BEOL Dielectrics*, J.L. Lauer***, *J.L. Shohet,* University of Wisconsin-Madison*, Y. Nishi,* Stanford University*, A. Antonelli*, Novellus Corporatiion

The minimum spacing between conductive lines in advanced integrated circuits (ICs) continues to decrease with each generation of technology. As a result, the long-term reliability of ICs is becoming increasingly dependent on the reliability of the intermetal dielectrics which often become damaged during back-end-of-the-line (BEOL) processing. Dielectrics used in BEOL structures are often irradiated with photons of various energies during plasma processing, charge annealing, and curing of porous materials. In particular, processing plasmas produce significant amounts of vacuum ultraviolet (VUV) radiation which are, among other processes, capable of creating electron-hole pairs within dielectrics. As a result, VUV radiation has an impact on the electrical conductivity of dielectrics during plasma processing which can either contribute to or mitigate trapped charge within dielectrics. We compare the charging response of 50, 250, and 450 nm of SiOCH, SiN, SiCO, SiCN, and SiC dielectrics on Si substrates after irradiation to vacuum ultraviolet (VUV) radiation. We choose to irradiate the dielectric layers to a photon energy of 9.5 eV because photons with this energy are often emitted from processing plasmas that contain oxygen, i.e. ashing and etching plasmas. The charging response of the dielectrics was evaluated by measuring the surface potential on the dielectrics with a Kelvin probe after irradiation with several doses of 9.5 eV photons. The surface potential on all of the dielectrics after VUV irradiation was positive due to the accumulation of positive charge by traps located within the dielectrics. By comparing the surface potential on several thicknesses of dielectrics after VUV irradiation we can estimate the location within the dielectric the charge is trapped. The surface potential on SiOCH layers of varying k-values after VUV irradiation indicates the presence of both negative- and positive-charged traps. From VUV-spectroscopy, we determined the SiOCH layers have electron traps located 0.8 eV below the conduction-band edge and hole traps located 1.4 eV above the valence-band edge.

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.

Plasma Science and Technology
Room: B2 - Session PS2-ThA

Plasma Diagnostics, Sensors, and Control II
Moderator: C.A. Wolden, Colorado School of Mines

2:00pm **PS2-ThA1 Absorption Spectroscopy Diagnostics of a Dual-Frequency Capacitive Dielectric Etch Tool using Ultraviolet Light-Emitting Diodes**, ***J.-P. Booth***, CNRS/Ecole Polytechnique, France, *J. Bredin*, LPP, France, *G.A. Curley*, LPN/CNRS, France

Dual–frequency capacitively-coupled etch reactors using Ar/fluorocarbon/O_2 mixtures are widely employed for etching of dielectric films for integrated circuit manufacture. CF_x free radicals play an important role in the gas-phase and surface chemistry controlling etching and polymer deposition. The CF_2 radical is the most abundant, and its density can be measured by UV absorption via the A-X band (230-270 nm). Previously Xe arc lamps have been used for the absorption light source, but these sources are rather unstable, limiting the sensitivity of the technique, as well as being cumbersome and relatively expensive. We have successfully replaced the Xe arc with UV light-emitting diodes. The baseline stability is of the order $2x10^{-4}$, compared to $1x10^{-3}$ with an arc lamp. We determined the variation of the CF_2 density as a function of gas composition and power in a modified 2 + 27MHz commercial etch reactor operating in $Ar/C_4F_8/O_2$. As expected, the CF_2 density decreases rapidly as the O2/C4F8 ratio is increased. The CF_2 density increases with RF power at both frequencies, but is most affected by 27 MHz power. There is speculation that CF_2 may play an important role in either or both the creation and destruction of F- negative ions. However, we did not find any simple correlation between CF_2 density and electronegativity (as determined from electron density and ion flux measurements).

We also attempted to measure the F^- negative ion density by the continuum absorption below 365 nm. However in this case we observed a broad but structured absorption when the O2/C4F8 ratio is small. This absorption is too intense to be attributed to F^-, and we speculate that it is due to unsaturated CxFy oligomerisation products.

We wish to thank the Lam Foundation for financial support.

2:20pm **PS2-ThA2 On-wafer Monitoring for UV/VUV Photon Irradiation during Plasma Processes**, ***B. Jinnai***, *S. Fukuda, H. Ohtake*, Tohoku University, Japan, *E.A. Hudson*, Lam Research Corp., *S. Samukawa*, Tohoku University, Japan

Plasma processes are indispensable for the fabrication of ULSI devices. In plasma, there are many activated species, such as charged particles, radicals, and photons. By using these species, etching and film deposition can be achieved. UV/VUV photon irradiation from plasma can cause serious problems because UV/VUV photons can be absorbed in films and generate defects, which may cause degradations of device characteristics. In order to overcome this issue, it is important to understand characteristics of UV/VUV photon irradiation from plasma, such as UV/VUV spectrum and its absolute intensity (photon flux). To investigate these characteristics of UV/VUV photon irradiation from plasma, a VUV spectrograph can be used. A VUV spectrograph is, however, generally expensive and large system, so it is difficult to install. Also, spectra data obtained from a spectrograph is not always corresponding to the information of UV/VUV photon irradiation incident to wafers, due to the different field of view. In this study, we measured plasma properties on a commercial capacitively-coupled dielectric etch reactor using a VUV spectrograph and our developed on-wafer monitoring technique. The on-wafer measurement is based upon plasma-induced current in SiO2 and SiNx thin films. Furthermore, we develop the neural network (NN) modeling method based on the data from our developed on-wafer monitoring technique. By using this method, we could successfully predict the profiles of the UV/VUV spectrum. From the current measured by the on-wafer monitoring technique, we calculated the absolute intensity of UV/VUV photons. The on-wafer monitoring technique has many advantages for the investigation of UV/VUV photon irradiation during plasma processes, and can be applied to the prediction of device damages induced by UV/VUV photon irradiation from plasma.

2:40pm **PS2-ThA3 Influence of Argon Metastables on the Rotational Temperature of Nitrogen in Inductively Coupled Ar/N_2 Plasmas**, ***J.-S. Poirier***, *J. Margot, L. Stafford, P.-M. Berube*, Universite de Montreal, Canada, *M. Chaker*, INRS-EMT, Canada

In low-pressure discharges commonly used for materials processing, neutral gas temperature are routinely determined from the rovibronic structure of N_2 inserted as a tracer. This is realized by comparing the measured emission intensities of the bandhead and the violet-degraded tail of the second positive system of N_2 ($C^3\Pi_u$ v' -> $B^3\Pi_g$ v'') to the prediction of a model with the rotational temperature, T_{rot}, as the adjustable parameter. Such measurements are usually performed using the most intense (v',v'')=(0,0) and (0,2) bands at 337.1 and 380.5 nm. However, in argon-containing plasmas, these bands typically yield temperatures larger than those obtained from other methods such as Doppler-shifted laser-induced fluorescence (D-LIF). Hypotheses for such discrepancy vary; either the emitting $C^3\Pi_u$n'=0 level (11.026 eV above the ground state) could be populated by the $^3P_0$ and $^3P_2$ argon metastables (11.723 and 11.548 eV above the ground state) or the spatial non-uniformity of the plasma could skew D-LIF measurements. In this work, we examined the influence of Ar metastables on the rotational temperature of N_2. We compared T_{rot} values obtained from different N_2 bands, notably (0,0), (0,2), (1,0), and (4,2) to a less conventional plasma sampling mass spectrometry (PSMS) technique in which the Ar plasma on-to-plasma off signal intensity ratio is linked to the gas temperature. These measurements were performed in an inductively coupled 98%Ar/2%N_2 plasma as a function of pressure and absorbed power. We show that N_2 bands with $v' \leq 2$ generated much higher T_{rot} values than the (4,2) band or the PSMS. For example, for a 20 mTorr, 1000 W Ar plasma, the (0,0), (0,2), (1,0), (4,2), and PSMS yielded temperatures of 973, 715, 920, 485, and 415 K, respectively. We then computed the reaction rates for excitation of the $C^3\Pi_u$ v'=0 level by collisions with Ar metastables, R-Ar^m, and by electron-impact, R-e, from the ground state. The densities required as inputs for those calculations were measured by Langmuir probe for electrons and, for the metastables, were determined from a global model. We found that that the ratio of the temperatures obtained from the (0,0) and (1,0) bands to that of the (4,2) band increased quasi-linearly with the R-Ar^m-R-e ratio, going from 1.5 to 2 as the Ar metastable-to-electronic excitation rate ratio increased from 0.01 to 0.1. Since Ar metastables can have a strong influence on rotational temperatures even for R-Ar^m-R-e ratio as low as 0.01, accurate gas temperature measurements in mostly Ar plasmas thus require analysis of bands for which $v' \geq 3$ as these levels (e.g. 11.74 eV for $C^3\Pi_u$ v'=4) are above the $^3P_0$ Ar metastable level.

3:00pm **PS2-ThA4 Electron Temperatures and Electron Energy Distribution Functions in Dual Frequency Capacitively-Coupled CF_4/O_2 Plasmas, Measured with Trace Rare Gases-Optical Emission Spectroscopy (TRG-OES)**, ***Z.Y. Chen***, *V.M. Donnelly, D.J. Economou*, University of Houston, *L. Chen, M. Funk, R. Sundararajan*, Tokyo Electron America

Dual-frequency capacitively coupled plasmas (2f-CCP) used in the fabrication of modern integrated circuits may provide quasi-independent control of ion flux and energy. The accurate determinations of the electron temperature (T_e) and the electron energy distribution function (EEDF) are important for understanding plasma behavior and optimizing plasma processes in 2f-CCPs. In this study, measurements of T_es and EEDFs in CF_4/O_2 plasmas generated in a 2f-CCP etcher were performed as a function of pressure, applied RF power, and O_2 feed gas content by using trace rare gases-optical emission spectroscopy (TRG-OES). The parallel plate etcher was powered by a high frequency (60 MHz) "source" top electrode, and a low frequency (13.56 MHz) "substrate" bottom electrode. 80%CF_4+20%O_2 or 90%CF_4+10%O_2 plasmas were ignited at pressures ranging from 4 to 200 mTorr, top RF powers of 500 and 1000 W, four different bottom RF powers (0, 100, 300 and 500 W), and three different wafers (Si, Al and anodized Al). T_e was measured across the plasma at a height of 5 mm above the lower electrode. For Si substrates, T_e increased with increasing pressure between 4 and 20 mTorr (typically from 5 to 6.5 eV). The dependence of plasma electronegativity on pressure may be responsible for this behavior. T_e decreased rapidly with increasing pressure in the 20-60 mTorr range, and then slowly decreased with further increases in pressure to 200 mTorr, where T_e = 2.4 to 2.7 eV. Increasing the applied bottom RF power resulted in higher T_e, caused by enhanced stochastic heating of electrons with increasing low frequency voltage. Over the entire pressure range investigated, T_es in 90%CF_4+10%O_2 plasmas were similar to those in 80%CF_4+20%O_2 plasmas. The EEDFs exhibited bi-Maxwellian characteristics with an enhanced high energy tail, especially at pressures >20 mTorr. Different dependences of T_e on pressure and applied top and bottom RF powers were observed for Al and anodized Al wafers.

3:40pm **PS2-ThA6 Laser and LED based Optical Diagnostic Techniques Applied in Industrial Plasma Etch Reactors**, ***N. Sadeghi***, Université Joseph Fourier de Grenoble and CNRS-UJF-INPG, France, *G. Cunge, D. Vempaire, M. Touzeau, R. Ramos*, CNRS-UJF-INPG, France **INVITED**

External cavity tunable diode lasers (DL) and Light Emitting Diodes (LEDs) are cost effective and easy to use tools that can be easily implemented for the diagnostics of process plasmas. We have used these techniques to characterize plasmas produced in several industrial etch reactors (Applied Materials and LAM Research) and to better understand the interaction mechanisms of the plasma with surfaces present: wafers or/and reactor walls.

Using near infrared DLs, we deduce the gas temperature in different silicon etch plasmas (Cl_2, CF_4, SF_6,..) from the Doppler width of absorption lines from argon metastable atoms when traces of argon is added to the process gas [1]. Absorption and Laser Induced Fluorescence experiments with a blue DL permits to map up the angular dependent velocity distribution function of aluminum atoms sputtered from a RF biased Aluminum wafer under argon ion bombardment [2].

We have shown that the sensitivity of Broad Band Absorption Spectroscopy (BBAS) can be enhanced by at least one order of magnitude when a LED is used as a light source [3]. Thanks to the high stability of the LEDs, it is also possible to perform time-resolved measurements of radicals densities in pulsed plasmas [4]. With a 350 nm LED, the time variation of Cl_2 density down to 3 mTorr can be measured with a time resolution of about 10 millisecond [3]. With a 275 nm LED, we have measured the decay time in the afterglow of the BCl radical produced in BCl_3/Cl_2 plasmas. It has been shown that the main loss mechanism of BCl radical is its gas phase reaction with Cl_2 to form BCl_2 molecule [4].

[1] G. Cunge, R. Ramos, D. Vempaire, M. Touzeau, M. Nejbauer, and N. Sadeghi, JVST A **27**, 471 (**2009**)

[2] R. Ramos, G. Cunge, M. Touzeau, and N. Sadeghi, J. Phys. D: Appl. Phys. **41,** 152003 (**2008**)

[3] G.Cunge, D.Vempaire, M.Touzeau and N.Sadeghi, Appl. Phys. Letters **91**, 231503 (**2007**)

[4] D.Vempaire and G.Cunge, Appl. Phys. Letters **94,** 21504 (**2009**)

4:20pm **PS2-ThA8 Monitoring of Atomic H and Cl Surface Loss Kinetics by Time-Resolved Optical Emission Spectroscopy in an ICP Reactor used for Etching III-V Materials**, ***G.A. Curley***, *L. Gatilova, S. Guilet, S. Bouchoule*, LPN-CNRS Upr20, France

A study is undertaken of the loss mechanisms of H and Cl atoms in an inductively coupled plasma used for the etching of III-V materials for photonic device fabrication. A better understanding of these mechanisms may allow us to refine our previous kinetic models of Cl2/H2-based plasma used to anisotropically etch InP-based devices [1], and be useful for monitoring the reactor walls state. The study is also of interest for Cl2/HBr-based plasma chemistries.

The plasma phase is diagnosed using a time-resolved optical emission spectroscopy technique often referred to as pulsed induced fluorescence (PIF). In previous PIF studies, the plasma is pulsed with a standard TTL signal and a short probing pulse (0.05 to 1 ms) is added to scan the afterglow. In our case we extract the fluorescence signal directly from the rising edge of the plasma ignition and therefore only standard pulse operation of the RF generator is required.

In principle the evolution of various radical densities in the afterglow could be followed with the PIF technique by varying the duration of the interval between two successive pulses (the off time). In this study we monitor the evolution of hydrogen and chlorine radicals to deduce their surface recombination coefficients. The plasma is pulsed with an off-time ranging from 200 µs to 100 ms. The on-time is chosen for steady state conditions to be reached. The targeted pressure value lies in the range of 0.5 mTorr to 10 mTorr.

In the case of hydrogen, comparing the increase rate of H2 to the decay rate of H allows us to estimate if surface recombination mechanisms other than H(g) + H(s) -> H2 have to be considered. We therefore monitored both the H-alpha (656.3 nm) the Fulcher-alpha (602nm) line of H2. By pulsing the plasma with long off-times we can verify that emission from dissociative excitation of H2 is negligible under our experimental conditions.

The typical recombination coefficient of H in our reactor, with SiOAlCl passivated walls, has been found to be around 0.01. More interestingly the growth rate of H2 is at least two times higher than the decay rate of H. We will therefore discuss two possibilities that may explain this experimental observation:

1) the existence of a competing loss mechanism for H2;

2) the existence of another loss mechanism for H-atoms. This possibility was proposed in a study of the side-wall passivation of InP etched with Cl2/H2 chemistry [1], where H(g) + Cl(s) -> HCl was assumed to favor the removal of Cl from the passivation layer.

Finally, the PIF technique is evaluated for the first time in chlorine plasmas to deduce the surface loss coefficient of chlorine atoms.

[1] L. Gatilova et al, JVST A 27 (2009) 262

4:40pm **PS2-ThA9 Real Time Control of an Inductively Coupled Plasma Simulation**, ***B.J. Keville***, *M.M. Turner*, Dublin City University, Ireland

Process yield in many plasma assisted processes may be improved significantly by real time, closed loop control of certain plasma species. This paper describes the closed loop control of a low pressure, inductively coupled plasma simulation. The plasma simulation consists of a global model of the plasma chemistry coupled to an equivalent circuit. The equivalent circuit incorporates an impedance matching box and an model of power coupling from the antenna into the plasma which has been derived from the wave equation and the two term solution to the Boltzmann equation. In addition, mass flow controller models and gas flow transport delays are included in the simulation. The design of effective, real time, closed loop control algorithms is facilitated by simple, control-oriented, dynamical models of the relationship between actuators (inputs) and the process quantities to be controlled. The paper will indicate how the parameters of a control algorithm may be determined from the process model (model-based control) in order to guarantee a robustly stable closed loop response. In general, process measurements are noisy and may not provide direct estimates of process quantities to be controlled. For example, estimates of atomic oxygen density obtained from optical emission spectroscopy are ambiguous due to dissociative excitation. Furthermore, many process parameters such as wall sticking coefficients are extremely difficult to estimate and may change due to chamber seasoning. The paper will indicate how an optimal state estimator may be used to improve estimates obtained from optical emission spectroscopy and how such estimates may be used to adapt the control algorithm in real time in order to guarantee process stability despite changes in process parameters.

5:00pm **PS2-ThA10 Wafer Temperature Response During Plasma Etching and Applications to Chamber Matching**, ***J. Shields***, *C. Gabriel*, Spansion, Inc.

As dimensions shrink, wafer temperature plays an increasingly important role in plasma etch process control. Temperature, however, is usually only monitored indirectly by measuring the chuck temperature or the coolant temperature during processing. To address these issues, we have employed the wireless KLA SensArray Integral wafer to measure the actual wafer temperature at 65 locations during wafer processing in a dielectric etch chamber with three different RF frequencies available. The Integral wafer records the temperature up to several times per second on internal memory, which is then downloaded to a computer after processing is completed. We conducted tests with no RF power, to determine effect of upper electrode and lower electrode temperatures on the wafer. We then measured the temperature response under variable RF excitation conditions for three different process chemistries utilized for dielectric and organic etching. For each process chemistry, comparisions between different excitation frequencies and combinations of frequencies were performed. The dependence of wafer temperature average and uniformity on backside helium cooling was determined, including a series of tests with no backside helium to isolate the effect of just RF delivered power. Finally, the promising application of this technique to chamber matching activities was analyzed.

5:20pm **PS2-ThA11 Plasma Etch Chamber Wall Deposits – Impact on Etch Species Density and Evaluation of Cleaning Procedures**, ***D. Dictus***, *D. Shamiryan, V. Paraschiv, S. Degendt, W. Boullart, M.R. Baklanov*, IMEC, Belgium, *C. Vinckier*, KU Leuven, Belgium

During the last ten years there has been a growing awareness about the impact of the plasma etch chamber wall condition on the density of reactive species in the etch chamber. This is especially the case for ICP chambers at low pressure (5-80mTorr) where gas phase diffusion and recombination at the reactor wall can be a dominant loss mechanism for reactive species. The majority of the studies are carried out for reaction chambers, coated with SiOCl or CF_x -based polymers.

In this paper we expanded the study to metal deposits such as titanium and tantalum which are frequently used for metal gate application in front-end-of-line, or as hard mask material for low-k etching in back-end-of-line. Additionally we made an evaluation of the cleaning procedures to remove these metals from the reactor walls.

CF_x-based polymers where deposited by igniting a polymerizing plasma, while Si, Ti and Ta were deposited by etching Si, TiN and TaN, respectively, in $Cl_2/HBr/O_2$ plasmas. The composition of the chamber wall deposits was investigated by XPS analysis of so-called ‘floating samples’. Relative density variation of reactive species (Cl, Br, O and F) in “contaminated” chambers was analyzed by actinometry. For the actinometry experiments we added 5% Ar to respectively Cl_2, HBr, O_2 and SF_6 plasmas and we related the peak intensities to the Ar 750nm peak. Our results indicate that the effect of the metal deposits is very similar to the CF_x-based deposits. We can summarize this as a lowering of all tested species densities when the chamber walls contain metal(oxide) traces. By comparing our data with previously published results we can also estimate a recombination probability.

Next to the study on density variations of reactive species we investigated how these metals are best cleaned from the chamber walls. This is again done with actinometry, by comparing the data of 'clean' and 'coated' chamber walls. For CF_x based coatings and SiOCl coated chambers the cleaning procedure is well known and is mostly done with O_2 and SF_6 based plasmas respectively. For the metals however we found that titanium should be cleaned with Cl_2 plasma and for Ta we observed that none of the tested chemistries was able to quickly remove it. Since our XPS data indicate that the Ti and Ta on the walls is partially in the form of TiO_2 and Ta_2O_5 this is not a surprising result. Finally, we did observed that it's possible to clean both metals with BCl_3 or $SiCl_x$ containing plasmas but this is beyond the scope of this work.

Surface Science
Room: M - Session SS1-ThA

Nucleation and Growth - Metals
Moderator: G.F. Verbeck, University of North Texas

2:20pm **SS1-ThA2 Influence of Quantum Well States on the Formation of Surface Au/Pb Alloy in Pb/Si(111) Quantum Thin Films**, ***J.D. Kim***, *S.Y. Qin, A. Khajetoorians,* The University of Texas, Austin, *W.G. Zhu, Z.Y. Zhang,* Oak Ridge National Laboratory, *C.K. Shih*, The University of Texas, Austin

The thickness dependence of Au/Pb alloy formation on thin Pb quantum films is studied using *in-situ* low temperature STM/S. Sub-monolayer Au is deposited onto thin Pb films on Si(111) substrates. When Au deposition is carried out at low temperature (~100K), it is found that nano-islands with moire patterns form on top of Pb mesas. With annealing, these moire islands are transformed into three different types of Au/Pb surface alloys. Each type of alloy shows its unique electronic properties and can be clearly identified by STS. Interestingly, the formation of these alloys is directly related to quantum well states (QWS) of underlying Pb films. For thinner thicknesses of underlying Pb layers (below 12ML), it is also observed that the alloy formation probability has strong thickness preference.

2:40pm **SS1-ThA3 Far-From-Equilibrium Film Growth on Alloy Surfaces: Ni and Al on NiAl(110)**, ***Y. Han***, *D. Jing, B. Unal, P.A. Thiel, J.W. Evans*, Iowa State University

We have analyzed the deposition of Ni and Al on NiAl(110) surfaces by STM and by KMC simulation of multi-site atomistic lattice-gas modeling incorporating DFT energetics. The goal is to elucidate far-from-equilibrium growth of metal films on alloy surfaces, including self-growth of alloys. Deposition of Ni produces reversible formation of monolayer islands which have some preference for diagonal steps at 300K and which are distorted-hexagons at 400K. Deposition of Al at 300K produces irreversible formation of irregular monolayer islands perhaps favoring steps in the [-110] direction. These features are recovered by the modeling, which elucidates the distinct nature of terrace diffusion of Ni versus Al on NiAl(110), the details of island nucleation, and the complexity of edge diffusion which controls island growth shapes. Additional studies of sequential co-deposition reveal "history-dependent" structures far from perfect equilibrium alloy ordering. Depositing Al first then Ni creates monolayer islands with a core of Al surrounded by a ring of Ni (although intermixing may occur at the interface). In contrast, depositing Ni first then Al creates monolayer Ni islands with significant second layer population by Al (reflecting stronger binding of Al on top of the Ni islands versus on NiAl(110) according to DFT).

3:00pm **SS1-ThA4 Growth Instabilities on Cu Vicinals: Metallic Impurities**, ***R. Sathiyanarayanan***, University of Maryland, College Park, *A. Bhadj Hamouda,* University of Monastir, Tunisia, *A. Pimpinelli,* Univ. B–Pascal Clermont-2, France & Science Attaché, French Embassy, Houston, *T. Einstein*, University of Maryland, College Park

Spontaneous pattern formation through kinetically controlled epitaxial growth provides a viable route for nanostructuring of surfaces. Ernst and co-workers found that during growth, Cu(100) undergoes a mounding instability, and its vicinal surfaces develop a meandering instability.[2] More specifically, (i) the meandering wavelength (λ_m) scales with deposition rate (F) as $\lambda_m \sim F^{\gamma}$, with $\gamma \approx 0.19$, (ii) both close-packed <110> and open <100> steps undergo meandering instability and (iii) above 10ML deposition, small pyramids appear near the steps. No previously-known instability mechanism, (esp. Bales-Zangwill, kink Ehrlich-Schwoebel effect, or unrestricted step-edge diffusion) could account for all of the experimental observations.

Using kinetic Monte Carlo simulations, A. Ben-Hammouda *et al.* showed that impurities codeposited on the surface could reproduce the λ_m–F scaling behavior and the formation of small pyramids.[3] Further, they found that only those impurity atoms (i) whose bond to Cu adatom is about 1.6 times the strength of the Cu-Cu bond and (ii) whose diffusion barrier is about 1.6 times the barrier of Cu adatom could cause the observed instabilities. Due to their stronger bonds with Cu adatoms, impurity atoms hinder Cu adatom diffusion, thereby shortening the diffusion length and making λ_m less sensitive to deposition rate (F). Also, impurity atoms act as nucleation centers for the formation of small pyramids.

By computing the binding energies and diffusion barriers for certain candidate impurity atoms, we could eliminate several species as possible sources of the observed instabilities. Using density-functional theory (DFT)-based Vienna *Ab-initio* Simulation Package (VASP), we computed the adsorption energies and diffusion barriers for many candidate impurity atoms. Our calculations show that common impurities such as oxygen, sulfur, and carbon actually repel Cu adatoms. The bonds formed by elements that alloy with Cu, e.g. Zn, Ag and Sn, are too weak to cause the observed instabilities; also, these atoms have smaller diffusion barriers than Cu. Our results indicate that either Fe or Mn atoms are causing the observed instabilities.[4] We discuss the results of our calculations and the possible role of impurities in nanostructuring of surfaces.

[1] Supported by NSF MRSEC Grant DMR 05-20471; NSF supported computer usage at NCSA, UIUC.

[2] N. Néel *et al.*, J. Phys.: Condensed Matter **15** (2003) S3227.

[3] A. Ben-Hammouda *et al.*, Phys. Rev. B **77** (2008) 245430.

[4] R. Sathiyanarayanan *et al.*, in preparation.

3:40pm **SS1-ThA6 Epitaxial Thin Films and Multilayers: Growth Mode, Microstructure and Physical Property Correlations**, ***R.A. Lukaszew***, College of William and Mary **INVITED**

The nucleation and growth mode of thin films determines their microstructure and also many of their physical properties, as for example the magnetic anisotropy in the case of epitaxial magnetic thin films. It is also possible to make artificial multilayers via deposition of subsequent layers of different materials and the microstructure and morphology of the intervening layers and interfaces determines many of the final structure properties.

Artificial metallic superlattices are multilayered thin films prepared by alternately depositing two or more elements epitaxially using ultra-high vacuum deposition or sputtering techniques. The concept of the superlattice was originally developed by physicists Leo Esaki and Raphael Tsu, who were both working at the IBM T. J. Watson Research Center in the 1960s.

Since then a wide spectrum of elements and compounds have been found suitable for deposition into multilayers and superlattice structures. The range of properties displayed by the resulting structures is greatly dependent upon the properties of both individual lattices as well as the interaction between them. For example, multilayers composed of magnetic and non-magnetic materials behave differently than the bulk materials and demonstrate a multiplicity of couplings between the magnetic layers. These couplings can be manipulated by choosing different layer materials and modifying their thicknesses. In fact the Giant Magneto Resistance (GMR) effect was found through such combinations and its discovery led to a Nobel Price in Physics.

In this talk I will present our studies on nucleation and growth of metallic and magnetic layers and the correlation observed between their microstructure and some of their unique physical properties.

4:20pm **SS1-ThA8 Nucleation and Growth of Ceria-supported Pt-Au Bimetallic Nanoparticles**, *Y. Zhou,* ***J. Zhou***, University of Wyoming

Ceria-supported metal particles have been under intensive study for their potential applications in fuel cells owing to the peculiar redox properties and oxygen storage capacity of ceria as well as the synergistic effect between the metal and ceria. Of particular interest are bimetallic systems because they can also exhibit unusual chemical and catalytic properties compared to the individual metals due to the synergistic effect between the two metals. To elucidate the nature of their chemistry in fuel cell applications, it is of significance to gain a fundamental understanding of their nucleation and growth processes on ceria supports. Here we report our recent study of bimetallic Pt-Au deposited on fully oxidized CeO_2(111) and reduced CeO_x(111) thin films using scanning tunneling microscopy and x-ray photoelectron spectroscopy. Ceria thin films with controlled degrees of cerium reduction were grown in situ on Ru(0001) under ultrahigh vacuum conditions. Pt and Au were vapor-deposited onto ceria thin films. Our study demonstrates that the growth and sintering behavior of Pt-Au bimetallic particles is dependent on the Ce oxidation states, metal compositions, as well as the metal deposition sequence. The growth of Pt-Au on well-ordered CeO_x(111) thin films was compared to that of pure Pt and pure Au as well as to that of bimetallic Pt-Au supported on nanocrytalline ceria surfaces. The research is sponsored by the start-up fund at University of Wyoming and the Wyoming NASA Space grant.

4:40pm **SS1-ThA9 Growth of Iridium on Ge(111) Studied by STM and LEEM**, ***C. Mullet***, *S. Chiang, J. Morad, A. Durand*, University of California, Davis

Iridium on germanium is a system which is useful for understanding the interaction of 5d metals with semiconductors, with potential applications to electronic contacts. We have used both scanning tunneling microscopy (STM) and low energy electron microscopy (LEEM) to characterize the submonolayer growth of iridium onto Ge(111) as a function of coverage, deposition temperature, and annealing temperature. Ir deposited onto the Ge(111) c(2x8) surface forms a $(\sqrt{3}\mathrm{x}\sqrt{3})\mathrm{R}30^{\circ}$ phase with the island size dependent upon substrate temperature during deposition. Deposition at a sample temperature of 670 C yields large micron-sized regions of continuous $(\sqrt{3}\mathrm{x}\sqrt{3})\mathrm{R}30^{\circ}$ coverage, as seen by LEEM. Deposition at 400 C produces Ir islands of three different sizes, all of which are too small to be resolved in LEEM but can be easily observed in room temperature STM images: large islands of roughly 10 to 20 nm diameter, consisting of multiple layers; medium-sized islands of roughly 4 nm in diameter, and small islands about 1 nm in diameter. The medium sized islands show a preference for growing at the bottom edges of steps. The small islands show a nearly uniform distribution on the sample surface, with the interesting exception of preferentially ordering in arrays of lines connecting medium-sized islands. Heating the sample over 640 C yields islands of large enough size to be resolved with LEEM, with the island size dependent upon annealing temperature. Ostwald ripening was observed in LEEM movies. When these large islands form during sample heating, they appear to 'avoid' areas of high step density near surface defects. At 840 C, desorption begins from these types of regions.

5:00pm **SS1-ThA10 Adatom- and Addimer-Mediated Exchange Diffusion of Embedded Ge Atoms in the Ge/Si(001) Surface Alloy**, *E. Bussmann*, ***B.S. Swartzentruber***, Sandia National Laboratories

Using low-bias empty-state STM images, we can resolve the location of embedded Ge atoms in the Ge/Si(001) surface alloy. We directly observe the diffusion of these embedded atoms at elevated temperatures (>100°C). That the diffusion of the embedded Ge atoms occurs in time bursts, is spatially correlated, and results in long displacements implies that the process is defect mediated. The responsible defects are adsorbed monomers and dimers. We have identified two exchange-diffusion pathways for the movement of the embedded Ge atoms, both of which are consistent with previous first-principles calculations [1, 2]. Adsorbed monomers of Si or Ge can readily place exchange with surface atoms as they anisotropically diffuse along the substrate dimer rows. These monomer exchange events are strongly correlated with common trap sites for monomers, such as, the ends of dimer rows of islands. Less frequent events are associated with adsorbed dimers that can exchange one of their atoms with a surface atom. That is, an adsorbed Si-Si dimer can exchange one of its Si atoms with an embedded Ge atom to become a Si-Ge dimer, which can subsequently re-exchange the Ge atom into the surface at a different location. Because the barrier for exchange in both of these pathways is only slightly higher than that for diffusion, Ge deposition on Si(001) leads to intermixing and surface-alloy formation at any temperature where diffusion is active. Sandia is a Lockheed Martin Company, operated for the U.S. DOE under Contract DE-AC04-94AL85000. This work was supported in part by the Division of Materials Science and Engineering, Office of Science, U.S. DOE, and was performed at the Center for Integrated Nanotechnologies, a U.S. DOE-BES user facility.

[1] Lu *et al.*, Surf. Sci. Lett., **506**, L282 (2002).

[2] Zipoli *et al.*, APL, 92, **191908** (2008).

5:20pm **SS1-ThA11 Substrate Effect on the Morphological Transition of Planar Magic Ag Nanoclusters**, ***Y.P. Chiu***, *B.C. Huang, C.Y. Shen*, National Sun Yat-sen University, Taiwan

Two-dimensional (2D) magic Ag nanoclusters have been demonstrated experimentally[1]. Experimental observations show that a template that originates from the electronic effect of quantum Pb islands grown on an Si(111) substrate can be used to develop Ag nanoclusters in planar feature with unusual size distributions, called a two-dimensional magic Ag nanocluster. Theoretically, the transition of Ag clusters from planar to 3D structures begins with Ag clusters of seven atoms without consideration of the substrate support [2]. However, utilizing the symmetry and size of the periodic pattern on the Pb islands, distinguishable planar hexagonal Ag clusters can be grown even for Ag clusters of 127 atoms [3]. How the substrate has influence on the morphological transition of Ag clusters from planar to 3D is of our interest and motivates the present work. To elucidate the effect of the substrate on the growth behavior of Ag clusters, highly oriented pyrolytic graphite (HOPG) is adopted as a template in the work. STM is used to characterize and analyze the growth behavior of Ag nanoclusters on HOPG. The process of the transition of Ag nanoclusters from planar to 3D and the onset of the formation of three-dimensional Ag clusters are also elucidated. A thorough analysis of the energetic optimization of Ag clusters not only yields information on the growth of Ag clusters on HOPG, but also elucidates how the substrate influences the formation of magic Ag clusters.

References

[1] Y.P. Chiu, L.W. Huang, C.M. Wei, C.S. Chang, and T.T. Tsong, Phys. Rev. Lett. **97,** 165504 (2006).

[2] Eva M. Fernández, José M. Soler, Ignacio L. Garzón, and Luis C. Balbás, Phys. Rev. B **70**, 165403 (2004).

[3] Y.P. Chiu, C.M. Wei, and C.S. Chang, Phys. Rev. B Vol. **78,** 115402 (2008).

Surface Science
Room: N - Session SS2-ThA

Supramolecular Interfaces by Design
Moderator: Y. Chabal, University of Texas, Dallas

2:00pm **SS2-ThA1 Cyano-directed Self-assembly of n-modular Porphyrin Oligomers at Surfaces: The Delicate Balance Between Competing Interactions**, ***N.P. Reynolds***, The University of Basel, Switzerland, *L.-A. Fendt*, ETH Zurich, Switzerland, *M. Stöhr, N. Wintjes, M. Enache,* The University of Basel, Switzerland, *T.A. Jung,* Paul Scherrer Institute, Switzerland, *F. Diederich*, ETH Zurich, Switzerland

The self-assembly properties of two cyano (CN) functionalized porphyrin isomers on Cu(111) were studied at different coverages by means of scanning tunneling microscopy (STM). Both isomers have two voluminous 3,5-bis(*tert*-butyl)phenyl substituents and two rod-like 4-cyanobiphenyl substituents in *cis* and *trans* configurations. For coverages up to one monolayer, the *cis* porphyrins were found to form a variety of oligomeric clusters ranging from dimers to hexamers, held together by cyanophenyl directed anti-parallel dipole-dipole interactions, hydrogen bonding and metal complexation. Furthermore, small changes in preparation conditions were also found to have a profound effect on the size distribution of the clusters. This variety and size distribution of the oligomers demonstrates how the delicate balance between the strength of absorbate-adsorbate and adsorbate-substrate interactions has a major effect on self-assembly.

Previous work from Yokoyama *et al.*1, using a similar molecule with shorter cyanophenyl binding groups formed exclusively tetrameric structures on less reactive Au(111) substrates. In this study high resolution STM images showed the presence of structures ranging from dimeric to hexameric, as well as chainlike structures. On the basis of this data we conclude that on the more reactive Cu(111), the very strong adsorbate-substrate interactions present are the dominating influence, leading to the multimorphism of binding motifs and oligomers observed.

[1] T. Yokoyama, S. Yokoyama, T. Kamikado, Y. Okuno, S. Mashiko, *Nature* **2001**, *413*, 619-621.

2:20pm **SS2-ThA2 The Directed Assembly of TiOPc - $\mathbf{C_{60}}$ Films: Three Structural Motifs**, ***Y. Wei***, University of Maryland, *S. Robey,* National Institute of Standards and Technology, *J. Reutt-Robey*, University of Maryland

A key strategy for the improvement of organic electronic devices involves the optimization of chemical morphology on the interfaces of donor-acceptor heterojunctions for efficient charge separation. Fundamental studies of chemical morphology - electronic property relations, particularly along crucial domain boundaries, are needed to realize these goals. We present STM/STS studies of TiOPc: C_{60} films, prepared in three dramatically different structural motifs: (1) Nanophase segregated TiOPc and C_{60} domains, (2) A co-crystalline $\mathrm{TiOPc}_{(2)}\ \mathrm{C}_{60\,(1)}$ honeycomb network and (3) A regular array of triangular TiOPc domains and C_{60} nanoclusters with a 10 nm repeat. Motif selection is accomplished through anisotropic TiOPc-TiOPc interactions, under the process control of TiOPc deposition rates. Subsequent C_{60} deposition on these pre-engineered TiOPc films yields these three distinct structural motifs. Chemical morphology-electronic relations are then determined via Z (V) STS spectroscopy. Electronic transport gaps vary weakly (~0.2 eV) by C_{60}-TiOPc phase. Significantly, an ~0.5 eV increase in the transport gap appears along heterointerface boundaries. We present structural models for each hetero interface and discuss the physical origin of the observed transport characteristics.

This work has been supported by the National Science Foundation under Surface Analytical Chemistry grant CHE0750203 and the Dept. of Commerce through the NIST small grants program.

2:40pm **SS2-ThA3 Supramolecular Engineering in Two Dimensions**, ***J.V. Barth***, Technische Universität München, Germany **INVITED**

The application of biologically inspired organization principles to artificial environments opens up intriguing vistas for the design of complex interfaces. Here we focus on well-defined metal surfaces serving as platforms to handle molecular building blocks with specific functionalities. We employ scanning tunneling microscopy for molecular-level imaging of both single molecules and self-assembled systems, whereas scanning tunneling spectroscopy captures the pertaining electronic properties. Distinct nanoarchitectures, such as biomoleular gratings, metal-organic arrays and porous nanomeshes, are realized through molecular recognition and selective hydrogen bonds, zwitterionic or metal-ligand interactions. Complementary insight from space-averaging techniques and computational modeling allows for the comprehensive assessment of structure-functionality correlation, notably including quantum confinement, chemical reactivity and magnetism. It is suggested that this supramolecular engineering strategy provides a versatile rationale to design unique nanosystems. Their tunable structural and functional characteristics bear promise for future technological applications.

3:40pm **SS2-ThA6 Fuctionalized C60 SAMs Diversity Via Molecular Conformation Variability**, ***B. Diaconescu***, University of New Hampshire, *T. Yang,* 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. Self-assembled monolayers (SAMs) form as a result of a delicate balance between competing molecule-substrate and intermolecular interactions. In order to control such self-organization processes, it is crucial to understand how this balance reflects onto the SAM's equilibrium structure. We will present a STM/DFT study of the self-assembly of C60 functionalized with alkyl chains of various lengths (F-C60) on Ag(111). We find that various structures are forming as a function of the alkyl chain lengths, ranging from zigzag to linear arrays of C60 cages, and they are driven by molecular conformational changes induced by the interaction with the surface. The symmetry of the F-C60 SAM is dictated by the molecular conformation, a consequence of molecule-surface interaction, while the size of the unit cell is a consequence of the intermolecular interactions. These results show that C60s can be assembled in 2D and non-compact molecular arrays with a unit cell symmetry and size controllable via appropriate chemical functionalization.

4:00pm **SS2-ThA7 Electronic Confinement Imposed by a Nanoporous Supramolecular Network**, *M. Matena, J. Lobo-Checa, M. Wahl,* University of Basel, Switzerland, *H. Dil,* University of Zürich, Switzerland, *L.H. Gade,* University of Heidelberg, Germany, *T.A. Jung,* Paul Scherrer Institute, Switzerland, *J. Zegenhagen,* ESRF, France, ***M. Stöhr***, University of Basel, Switzerland

Molecular assemblies on surfaces can be used as templates that allow the study of host guest interactions and provide in a further step an ideal starting point for the generation of more complex hierarchic structures. An important prerequisite besides the regularity of such structures is their stability.

We reported the formation of a molecular honeycomb network generated by thermal dehydrogenation of a perylene derivative (DPDI) on a Cu(111) surface [1]. By thermal activation, these molecules become H-bond donors/acceptors and form a highly regular honeycomb structure which is commensurate to the Cu substrate. This network can be used as a template for the incorporation of guest molecules in its hexagonal “holes” [2], [3]. Besides utilizing this network for the study of guest molecules, XSW (x-ray standing wave) experiments were carried out to gain more structural information and by this more information on the molecule substrate interaction. This is done by determining the vertical height of the molecules above the Cu surface before and after annealing the sample. Before annealing, the DPDI molecule is chemisorbed. It mainly interacts via its N atoms with the Cu surface and is in a bridge-like configuration. After annealing, the height difference between the end groups and the perylene core is lowered what is required to enable H-bonding between the molecules.

Furthermore, to study the interaction between the electronic Cu surface state and the DPDI network, scanning tunneling spectroscopy (STS) and angle-resolved photoemission spectroscopy (ARPES) were used. Each pore of our porous network confines the Cu surface state in what can be described as a 0D quantum dot. Due to the imperfect confinement observed for all 0D cases studied so far on surfaces, the quantum dots couple with their neighbors resulting in shallow dispersive electronic bands [4]. A consequence of this work is the perspective to engineer these artificially created electronic structures by modification of the dimensions of the molecular network periodicities together with the appropriate choice of the substrate.

[1] M. Stöhr et al., Angew. Chem. Int. Ed. 44 (2005) 7394; [2] M. Wahl et al., Chem. Commun. (2007) 1349; [3] M. Stöhr et al., Small 3 (2007) 1336; [4] J. Lobo-Checa et al., submitted.

4:20pm **SS2-ThA8 Surface Supported Chain Formation of Magnetic Molecules**, *S. Chang,* University of Hamburg, Germany, *K. Clark, A. Dilullo,* Ohio University, ***S. Kuck***, University of Hamburg, Germany, *S.-W. Hla,* Ohio University, *G. Hoffmann, R. Wiesendanger*, University of Hamburg, Germany

The last years showed a tremendous development into accessing and understanding the physics of metal-organic complexes in contact to a surface on a single molecule level. Molecular classes in the focus are often specialized but commercially available systems. Further progress towards device development requires molecular classes with a more flexible structure for functionalization.

In our contribution we introduce such a promising candidate, the so called Salens, and present first results on the local investigation by Scanning Tunneling Microscopy (STM). Salens are volatile metal-organic complexes with the metallic ion caged from three sides. Salens are chemically easily modified to tune the interaction with a substrate, with neighboring molecules, or to establish an intramolecular electronic and magnetic communication between two metallic centers through the organic periphery. Based on the paramagnetic Co-Salen, which shows no self-assembly on metallic substrates, we demonstrate that the exchange of a single atom in the molecular structure the interaction can be tuned from repulsive to attractive interaction[1]. Even surface-supported covalent bonding can be initiated to form larger entities. By means of STM, STS, and STM induced manipulation we will discuss the adsorption and the electronic properties of the parent Co-Salen and modified Salens on metallic and isolating surfaces.

Acknowledgements: This work was supported by the DFG within the GrK 611 and the SFB 668-A5, by the EU in the project “SPiDMe”, and the NSF-PIRE program.

[1] S. Kuck et al., “Steering two dimensional molecular growth via dipolar interaction“, accepted for publication in ChemPhysChem (2009).

4:40pm **SS2-ThA9 Reactive Adsorption to Ordered Bis-Terpyridine Networks**, ***T. Waldmann***, *H.E. Hoster,* Institute of Surface Chemistry and Catalysis, Germany, *D. Künzel,* Institute of Theoretical Chemistry, Germany, *M. Roos, A. Breitruck,* Institute of Surface Chemistry and Catalysis, Germany, *A. Groß,* Institute of Theoretical Chemistry, Germany, *R.J. Behm*, Institute of Surface Chemistry and Catalysis, Germany

Using time resolved scanning tunneling microscopy, we tested the effect of O2 exposure on ordered supra-molecular networks of Bis-terpyridine derivative molecules (2,4’-BTP)[1,2] supported on Au(111)[3], Ag(111) [3,4] and Graphite[3] (HOPG) substrates at T = 300 K. Under certain circumstances, our image sequences unambiguously show modifications of individual 2,4’-BTP molecules upon O2 exposure and concomitant re-arrangements within the hydrogen bonded adlayer. Furthermore, comparison of the behaviour on different substrates clearly shows that these modifications require a catalytically active surface.

The experimental observations are complemented by density functional theory calculations. In combination, both give rise to a probable model for the observed surface reactions and their effect on the supramolecular structure.

[1] U.Ziener et al., Chem.Eur.J. 8, 951, 2002

[2] C. Meier et al., J.Phys.Chem.B 109, 21015, 2005

[3] H.E. Hoster et al., Langmuir 23, 11570, 2007

[4] M.Roos et al., Phys. Chem. Chem. Phys. 9, 5672, 2007

5:00pm **SS2-ThA10 Charge Transfer-Driven Molecular Self-Assembly at Organic/Metal Interfaces**, *T.-C. Tseng,* Max Planck Inst. for Solid State Res., Germany, *C. Urban, W. Yang,* Univ. Autonoma de Madrid, Spain, ***R. Otero***, UAM & IMDEA-Nano, Spain, *S.L. Tait,* Max Plank Inst. for Solid State Res., Germany, *M. Alcami, D. Ecija, M. Trelka,* Univ. Autonoma de Madrid, Spain, *J.M. Gallego,* ICMM-CSIC, Spain, *M.A. Herranz,* Univ. Complutense de Madrid, Spain, *F. Martin,* Univ. Autonoma de Madrid, Spain, *N. Martín,* Univ. Complutense de Madrid, Spain, *K. Kern,* Max Plank Inst. for Solid State Res., Germany, *R. Miranda*, UAM & IMDEA-Nano, Spain

Organic heterostructures based on blends of molecules with electron-accepting (large electron-affinity) and electron-donating (small ionization potential) character display interesting electrical and optical properties with promising technological applications. For example, they show electroluminiscence for Organic Light Emission Diodes (OLEDs), photovoltaic response for solar cell devices and one-dimensional conduction for low molecular-weight metallic films, while strong acceptors or donors are the basis for metal-organic magnets. These blends of molecules are deposited onto or contacted with metallic layers and their performance depends crucially on the alignment of energy levels, the molecular nanostructure and crystalline perfection. Interfaces between organic species with either donor or acceptor character and metal surfaces are, thus, of paramount importance for the performance of the devices described above. This observation has motivated a large effort aimed at understanding the electronic structure of organic/metal interfaces and, in particular, the alignment of the energy levels at the interface related to the charge transfer between the organic donor or acceptor species and the metallic surface. Charge transfer, however, not only leads to modiffcations in the alignment of energy levels; usually, it is also related to structural transformations in both donating and accepting species. Unfortunately, too often it is assumed that the substrate is just an inert spectator, playing no active role in the supramolecular organization. We describe here experiments (STM, LEED, XPS) and theoretical simulations that unequivocally demonstrate that for strong charge transfer systems, such as the organic acceptor tetracyanoquinodimethane (TCNQ) deposited on Cu(100) *both* the molecules *and* the substrate suffer strong structural rearrangements that may even control the resulting molecular ordering. Such charge transfer-induced structural rearrangements at both sides of the organic/metal interface might have signiffcant effects on the subsequent growth and structure of the organic film and, thereby, on device performance.

5:20pm **SS2-ThA11 Architectural Complexity, Intermolecular Interactions, and Charge Transfer in Supramolecular Networks at Surfaces**, *H. Adler, Y. Ge,* ***S.L. Tait***, Indiana University

Self-assembly of two-dimensional supramolecular networks stabilized by hydrogen bonding or metal—organic coordination offers an efficient route to the rational design of functional surface architectures and provides a model system for (bio-)molecular assembly. These systems may contribute to advances in sensors, catalysis, molecular electronics, photovoltaics, and other thin film device applications. Such systems have been demonstrated to form highly-ordered, extended networks by selective and directional coordination bonding. Experiments were made using metal atoms and organic ligands containing carboxylic acid, cyano or pyridyl functional end groups, which were vapor deposited to atomically clean and flat surfaces. Structural characterization by scanning tunneling microscopy allows molecular level insight into the structure and assembly of the systems. X-ray photoelectron spectroscopy provides evidence for chemical interactions within the networks. High-resolution electron energy loss spectroscopy lends insight into intermolecular interactions. These experiments are correlated with density functional theory calculations for a better understanding of the bonding interactions that stabilize the highly ordered surface nanostructures. Binary mixtures of ligands allow for a large variety of metal-organic frameworks based on hierarchical assembly, co-crystallization, or cooperative multi-ligand coordination interactions. Current studies are focusing on understanding chemical function of these systems and how this can be tuned through supramolecular design strategies.

Thin Film
Room: B4 - Session TF-ThA

Next Generation Processing
Moderator: S. Gupta, University of Alabama

2:20pm **TF-ThA2 Resonant Infrared Matrix-Assisted Pulsed Laser Ablation of Electroluminescent Dendrimer Thin Films**, ***R.D. Torres***, University of Florida, *S.L. Johnson,* Vanderbilt University, *J. Hwang,* University of Florida, *P.L. Burn,* University of Queensland, Australia, *R.F. Haglund,* Vanderbilt University, *P.H. Holloway*, University of Florida

The processing to create polymer thin films for organic light emitting diodes is limited to wet methods since molecular pyrolysis prevents the use of dry vacuum thermal evaporation methods. Wet methods have critical limitations such as poor thickness control, drying patterns, re-dissolution of previous layers, substrate limitations and others. In this work, a novel approach for the growth of thin polymer films, Resonant Infrared Matrix-Assisted Pulsed Laser Ablation (RIM-PLA), has been studied as a possible dry conformal deposition method for electroluminescent polymers. RIM-PLA was successfully used for the deposition of two model dendrimers: fluorescent and phosphorescent Ir-cored. A free-electron laser was tuned to the resonance frequency for the vibrational modes of two matrix solvents: toluene and chloroform. For chloroform, the alkyl C-H stretch (3.32 µm) and C-H bending (8.18 / 8.28 µm) modes were compared. For toluene, the C-H stretch (3.31 µm) and aromatic C=C stretch (6.23 µm) modes were compared. Targets made from flash-frozen, low-concentration solutions of the dendrimers were irradiated at each frequency while varying fluence and exposure times. The molecular structure integrity of the targets was characterized by NMR and FTIR spectroscopy, and MALDI-TOF spectrometry. The deposited film quality was characterized by surface roughness and topography measurements (AFM, stylus profilometry, optical/fluorescence microscopy), and luminance (photoluminescent spectra and quantum yields). The RIM-PLA deposited films were compared with films that were spin-coated from solution. It was found that the ablation characteristics of each mode were dependent on the solvent and not the dendrimer. Calculations from a thermal-rise model show that FEL pulsed-irradiation results in heating rates on the order of 10^8 – 10^9 K/s depending on the absorption coefficient of the selected mode. As a result, localized temperatures in the melted focal volume approach the solvent's superheat limit (~0.8 T_c), leading to spinodal decay and subsequent phase explosion. I.e. ablation occurs via a rapid spontaneous homogeneous nucleation of vapor bubbles within the melted solvent, which in turn develops a shockwave that propagates and ejects different size droplets from the target surface. The size and the frequency of the droplets depend on the absorption properties of the selected mode. The deposited films' characteristics correlate well with the thermal-rise model.

2:40pm **TF-ThA3 Etching Technology for Patterned Media used for Ultra High Density Hard Disk Drive**, *D.D. Djayaprawira,* ***Shinde***, Canon-ANELVA Corporation, Japan **INVITED**

Patterning of magnetic recording media is one of the proposed approaches for extending magnetic storage densities beyond 1Tbit/in2. This approach is based on patterning the recording media into magnetically separated areas, which can be used for storing a single bit of information. Here we introduce the etching technology and equipment for discrete track recording media (DTM) mass-production. A unique requirement for magnetic recording media patterning system is that the system should be able to etch both sides of the media. Furthermore, since a typical media sputtering time in a process chamber is less than 4 seconds, a reasonably high etching rate approach is necessary. To this end, we developed reactive ion etching (RIE) and ion beam etching (IBE) modules based on inductive coupled plasma (ICP) source. The advantages of using the ICP source are the high density plasma

and the plasma are confined within the cavity. The high density plasma contributes to high etching efficiency. The confined plasma minimized the interference of ICP sources and enable the mounting of RIE or IBE modules facing each other. Recent etching results using RIE and IBE modules will be presented, and the feasibility of our approach for mass-production of DTM will be discussed.

3:40pm **TF-ThA6 Resonant Infrared Pulsed Laser Deposition of Organic Materials for Display Applications**, ***H.K. Park***, AppliFlex LLC, *K.E. Schriver, R.F. Haglund*, Vanderbilt University

We report the resonant infrared pulsed laser deposition (RIR-PLD) technique for depositing novel, functional polymers, small organic molecules and nanoparticle-loaded polymers. Film deposition based on resonant infrared (RIR) laser ablation is enabled by resonant excitation of a localized, intra-monomer vibrational mode of the target material, such as a

C-H stretch; this leads to low-temperature volatilization and deposition of undamaged small molecules, polymers and even nanoparticles. Because the mid-infrared photons used in this process have energies far below those required to break the bonds that connect monomer units, RIR laser irradiation ablates polymers without photofragmentation, unlike ultra-violet pulsed laser deposition (UV-PLD). In this paper, we will demonstrate successful RIR-PLD deposition of selected materials that are essential to organic light emitting diode (OLED) technology; (1) light emitting small-molecule and polymer materials such as Alq_3 (Tris(8-hydroxyquinolinato)aluminium), MEH-PPV and conducting polymer PEDOT:PSS (Poly(3,4-ethylenedioxythiophene) poly(styrene sulfonate)); (2) polymeric barrier film such as cyclic olefin copolymer (COC) and Teflon®; and (3) nanocomposite materials based on TiO_2 and metal nanoparticles that serve as brightness enhancement layers and transparent conducting electrodes.

The deposited films are characterized by SEM (scanning electron microscopy) and FTIR (Fourier-transform infrared spectroscopy), photo- and electroluminescence. We will also present the comparison of film properties as they depend on different mid-infrared laser choices, such as a picosecond, tunable free electron laser (FEL), Er;YAG laser and picosecond optical parametric oscillator (OPO).

4:00pm **TF-ThA7 Room Temperature Synthesis of Silica and SiO_2-TiO_2 Composites for use as Barrier and Anti-Reflection Coatings**, ***P.C. Rowlette***, *C.A. Wolden*, Colorado School of Mines

Thin film oxides are ubiquitous in photovoltaics, serving as transparent electrodes, passivation layers, optical coatings, and moisture permeation barriers. Pulsed plasma enhanced chemical vapor deposition (PECVD) was used to deliver digital control of SiO_2, TiO_2, and $Si_xTi_yO_z$ composites at room temperature. Sub-angstrom control of SiO_2 deposition rate was demonstrated by varying the $SiCl_4$ density at low exposure levels (~250 L). No impurities were detected by XPS or FTIR, and the high film quality was confirmed by etch rate measurements. Crack-free SiO_2 films have been deposited on polymer substrates, and we are currently assessing their barrier performance.

Next, SiO_2-TiO_2 composites were formed by pulsed PECVD using $SiCl_4$ and $TiCl_4$ as precursors. The refractive index of the SiO_2-TiO_2 material system spans a large dynamic range (n: 1.4 – 2.4), and as such is of great interest for optical coatings. Alloy formation was investigated by maintaining constant delivery of one precursor while varying the second. Film composition was assessed by spectroscopic ellipsometry, XPS, and FTIR. It is shown that the alloy composition and refractive index can be tuned continuously over this broad range using pulsed PECVD. These two precursors were found to be highly compatible, with the alloy growth rate simply reflecting the sum of the contributions from the two individual precursors. The digital control over both thickness and composition offered by pulsed PECVD was demonstrated through room temperature synthesis of antireflection (AR) coatings for crystalline silicon solar cells. One, two, and three-layer AR coatings based on the range of indices offered by the SiO_2/TiO_2 system were designed and optimized to minimize the reflectance across the visible spectrum. AR coatings based on these designs were then fabricated, and in each case the measured optical performance was found to be in excellent agreement with model predictions. The integrated reflectance across the visible spectrum was reduced from 39% for uncoated wafers to 2.5% for the 3-layer AR coating.

4:20pm **TF-ThA8 Expanding Thermal Plasma Deposition of a-Si:H Thin Films for Surface Passivation of c-Si Wafers**, ***A. Illiberi***, *V. Verlaan, M. Creatore, W.M.M. Kessels, M.C.M. van de Sanden*, Eindhoven University of Technology, The Netherlands

We investigated the material properties of expanding thermal plasma deposited a-Si:H thin films, providing a record-low surface recombination velocity of 1.6 cm/s (at injection level of 1 10^{15} cm^{-3}). a-Si:H thin films with different thicknesses have been deposited at a high deposition rate (1.2 nm/s) on both sides of low resistivity (1-5 Ohm cm), 260µm thick, *n*- and *p*-type c-Si FZ wafers. The material properties of a -Si:H films have been characterized by Fourier Transform Infrared diagnostic and Spectroscopic Ellipsometry. The surface passivation of the wafers has been determined by photoconductivity decay measurements of the effective carrier lifetime. The investigation points out that the growth of ETP a-Si:H films begins with the formation of a thin porous layer (< 10 nm) with a refractive index of 3.9 (at 2 eV) and a microstructure parameter (R*) of 0.50. Despite the open network formation at the a-Si/c-Si interface, a 7 nm a-Si:H film achieves a recombination velocity as low as 12 cm/s (at $1{\cdot}10^{15}$ cm^{-3} injection level on n-type wafers). The good passivation is probably due to the large hydrogen content of the a-Si:H film, which terminates dangling bonds present on the c-Si surface. After this initial growth, a dense a-Si:H network develops with a refractive index of 4.3 (at 2 eV) and R* = 0.03. The surface recombination velocity decreases linearly with the a-Si:H thickness, achieving a record value of 1.6 cm/s (at $1{\cdot}10^{15}$ cm^{-3} injection level) for 90 nm thick a-Si film on n-type wafers. As compared to hot wire CVD and radiofrequency PECVD techniques, ETP is capable to deposit thin a-Si:H films with outstanding surface passivation at higher temperature (250° C) and higher deposition rate (1.2 nm/s). The stability in time of surface passivation has been investigated. Effective carrier lifetime is found to decrease following a stretched exponential. Photo-electronic properties of a-Si:H are know to relax in time in a similar fashion. These results therefore suggest a correlation between the photo-electronic properties of the a-Si:H/c-Si interface and a-Si:H bulk material.

4:40pm **TF-ThA9 Effect of Oxygen Incorporation on the Properties of CdS/CdTe Interface and the Device Properties**, ***R.G. Dhere***, *J.N. Duenow, S.E. Asher, Y. Yan, M. Young, T.A. Gessert*, National Renewable Energy Laboratory

The development of CdTe solar cells over the last 35 years has been advanced by introducing various modifications in the fabrication process such as post-deposition $CdCl_2$ heat treatment and CdS deposited by chemical-bath deposition (CBD). The presence of oxygen during various stages of CdTe/CdS device fabrication is also known to benefit device performance. The first devices reported by Kodak to have efficiencies greater than 10% were fabricated by close-spaced sublimation (CSS) in oxygen ambient. $CdCl_2$ heat treatment, crucial for achieving high efficiency, is usually carried out in ambient containing O_2. In previous studies on devices fabricated using CBD CdS, CSS, and sputtering, the interdiffusion at the CdS/CdTe interface was correlated to the presence of O_2 in CBD CdS. We have fabricated devices with sputtered CdS films that have efficiencies near 14%, comparable to our baseline devices using CBD CdS. In this paper, we present our recent work on CdTe devices using CdS prepared by sputtering and CBD. For sputtered CdS films, we varied O_2 content in the sputtering ambient from 0% to 3%. CdTe films were deposited by CSS in oxygen ambient and conventional physical vapor deposition in high vacuum. We will present detailed characterization of the CdS/CdTe interdiffusion at the interface. Specifically, we used secondary-ion mass spectrometry for samples fabricated under different conditions to investigate the dependence of interdiffusion characteristics on oxygen ambient during fabrication. We will also present the results of our transmission electron microscopy analysis on the structural properties of the CdS/CdTe interface and its correlation to the microstructure of CdS deposited by both techniques as well as oxygen in the fabrication process. We will fabricate devices using the samples from these studies and characterize the devices using standard current-voltage analysis. We will then analyze the results to correlate the device properties to the interface properties.

5:00pm **TF-ThA10 Large-Scale Simulations of Nanoimprint Lithography**, ***M. Chandross***, *G.S. Grest*, Sandia National Laboratories

The production of surfaces with controllable/tunable nanostructures over large areas and at throughputs practical for commercial applications can be very difficult. Two processes of recent interest have been step-flash imprint lithography (SFIL) and nanoimprint lithography (NIL) in which nanoscale masks are imprinted into polymeric materials to create features with nm-scale resolution. Empirical approaches are currently the norm for industrial scale-up but are often prohibitively time-consuming and expensive. Modeling and simulation can decrease manufacturing process design cycle time enormously, as has been proven in many industry segments.

Here we present our activities specifically with regard to nanopatterning by detailed large-scale simulations of nanolithographical processes in which rigid molds are imprinted into liquid oligomers that are subsequently hardened. We use a generic polymer model that can be applied to both SFIL, in which the oligomers are cross-linked by exposure to UV irradiation, and NIL, in which the liquid is hardened by lowering the temperature below the glass transition. Multiple stamps are inserted into melts of liquid oligomers at a temperature above the glass transition. The melts are either quenched or croslinked and the systems are equilibrated. Stamps are then either removed at constant velocity to study the effects of stress and adhesion on resulting features, or simply deleted to study the effects in the limit of zero stress. We vary the size and pitch of the stamps in order to study the resolution limits of both methods.

5:20pm **TF-ThA11 All through Stencil MOSFET Fabrication**, ***L.G. Villanueva***, *O. Vazquez-Mena,* EPFL, Switzerland, *J. Montserrat,* IMB-CNM-CSIC, Spain, *K. Sidler, V. Savu,* EPFL, Switzerland, *J. Bausells,* IMB-CNM-CSIC, Spain, *J. Brugger*, EPFL, Switzerland

The fabrication of micro and nano devices using standard processing techniques is mainly based on the pattern transfer of designs onto a substrate. These standard techniques use pre-patterned resists that selectively expose certain parts of the substrate either to material deposition or implantation or to an etching process. The use of resist processes implies the coating, exposure, development and removal of the resist and also imposes certain restrictions regarding the materials and substrates to pattern (e.g. only flat substrates are acceptable). An alternative to resist-based processes is the use of stencil lithography (SL), which relies on the use of a shadow mask membrane, and has already been proved to achieve sub-micrometer resolution for metallization, and more recently for direct-etching and ion-implantation. In this abstract we present the combination of the three mentioned techniques to fabricate Metal-Oxide-Semiconductor Field Effect Transistors (MOSFET).

The proposed fabrication process flow of the MOSFETs follows the basic stages (Figure 1 in supplementary information) starting with a 100 mm diameter p-doped silicon wafer in which the n-doped regions for Source-Drain definition are implanted *through stencil*. Subsequently, the gate oxide is grown in a process that also activates the impurities in the lattice. Contacts for Source and Drain are opened in the oxide by means of dry etching *through stencil* and, finally, metal pads are deposited *through stencil*. All the stencils used were fabricated using standard microfabrication techniques (i.e. resist based processes) in 100 mm diameter wafers. However, for better compatibility with the processing equipment during MOSFET fabrication, the wafers were cleaved and the stencils were used in chip size.

Different designs were included in the fabrication: resistors, transistors and NOR gates. In addition, to demonstrate the capability of SL to pattern non conventional substrates, the transistors were fabricated not only on flat substrates, but also at the bottom of pre-patterned steps of 40 µm and 100 µm (Figure 2 of supplementary information).

The characterization shows that resistors have a linear I-V behavior. The square resistance decreases with the gap as expected (Figure 3, supplementary information). In addition, transistors also show the expected behavior (Figure 4, supplementary information), with a well defined saturation region.

The presented technique proposes a new concept for the fabrication of electronic devices, allowing the fabrication of structures on pre-patterned surfaces with resolutions close to the micrometer, which can be of great utility for some specific applications.

Biomaterial Interfaces
Room: Hall 3 - Session BI-ThP

Biomaterial Interfaces Poster Session II (Arrays, Sensing, Micro/Nanofabrication, SPM)

BI-ThP1 Integration of Protein Microarrays and Glyconanoparticles with Surface Plasmon Resonance Imaging to Probe Carbohydrate-Protein Interactions*, **H. Wang**, X. Wang, M. Yan*, Portland State University

Multivalent interactions between carbohydrates and proteins are attracting increasing interest because of their importance in many biological processes. We developed a strategy integrating microarrays, nanoparticles and surface plasmon resonance imaging (SPRi) to study carbohydrate-protein interactions. Protein microarrays were fabricated and carbohydrate-coated glyconanoparticles were used as multivalent probes to target carbohydrate-binding proteins. SPRi offers a real-time sensing method to investigate multiple binding events simultaneously. The chemistry, fabrication and characterization of microarray platforms will be discussed. The binding parameters and SPRi responses with regard to surface chemistry and ligand density will be presented.

BI-ThP2 Aqueous Polymer Nanografting: AFM patterning of Poly-L-Lysine on Oxide Surfaces*, **B.S. Davis**, H.J. Conley, J.L. Knoebel, K.B. Hurd, J.N. Harb, M.R. Linford, R.C. Davis*, Brigham Young University

We present a scanning probe lithography technique that allows for patterning of adsorbed, water-soluble polymers on functionalized oxide surfaces. SiO_2 and borosilicate glass surfaces were functionalized with a negatively charged carboxyl-terminated silane monolayer. A ca. 2 nm poly-L-lysine layer was then deposited over the silane film. An atomic force microscope (AFM) probe was used to scribe away lines and areas of the positive poly-L-lysine layer, exposing the negatively charged silane underlayer. The AFM scribing experiments were performed both in air and in water. Regions were scribed and then backfilled with a fluorescently tagged polymer. Characterization of the scribing was done with tapping mode AFM. Optical fluorescence microscopy was used to image backfilled regions. AFM height and phase mode data showed lines and spaces with half pitch features as small as 12 nm created with a scribing force of 0.3 μN.

BI-ThP3 High Sensitivity Electrochemcial Immunosensor Based on Plasma Modified TiO_2/Chitosan*, R. Khan,* North East Institute of Science & Technology, India*, **M. Dhayal***, Centre for Cellular and Molecular Biology, India

RF plasma treated nanocrystalline hybrid chitosan/TiO_2 matrix was used to develop high sensitivity electrochemical immnunosensor. The observed interfacial charge transfer resistance (R_{CT}) and double layer capacitance (C_d) of plasma modified matrixes were decreased. An improved strength of amide I and II groups in FTIR spectra were observed which was associated with enhancement in immobilized rabbit antibodies (IgGs) on plasma altered surfaces. Electrochemically q uantitative detection of *Ochratoxin-A* (OTA) concentrations varying in buffer solution was carried out on IgGs immobilized plasma treated and untreated ITO/CS/TiO_2 electrodes. Plasma modified electrodes had showed very good sensitivity at very low OTA concentrations whereas the untreated electrodes sensitivity was deprived.

BI-ThP4 Measuring Magnetic Properties of Individual Magnetosomes by Scanning Transmission X-ray Microscopy*, **A.P. Hitchcock**, K.P. Lam, M. Obst,* McMaster University, Canada*, U. Lins*, Universidade Federal do Rio de Janeiro, Brasil

We have studied the Fe 2p X-ray magnetic circular dichroism (XMCD) of individual magnetosomes - biomineralized ferrimagnetic nano-crystals in magnetotactic bacteria (MTB) - using scanning transmission X-ray microscopy(STXM). Magnetosomes are intracellular magnetite (Fe_3O_4) or greigite (Fe_3S_4) nano-crystals (typically 30-60 nm in size), enclosed in a lipid membrane. A chain of magnetosomes is used by MTBs to orient relative to the earth's field, and guide motion to optimal living environments. Our initial goal, which has been achieved, was to demonstrate that the STXM has the capability to investigate magnetic properties of sub-50 nm areas in biological systems. The Fe 2p XMCD of individual Fe_3O_4 magnetosomes of MV-1, a marine vibrio species of magnetotactic bacteria, was measured with the sample at 30 degrees relative to the beam to sense the in-plane magnetic component. This is the first such measurement of the XMCD of a single magnetosome to our knowledge. Evidence for multiple domains was found in some magnetosomes. In addition we have begun to explore the associated biochemistry by STXM spectromicroscopy at high spatial resolution (30 nm) at the C 1s and O 1s absorption edges. The combined XMCD and biochemical imaging will help further the understanding of biomineralization processes present in MTB and other environmental organisms.

Research funded by NSERC. The Canadian Light Source is supported by NSERC, NRC, CIHR, and the University of Saskatchewan. Some measurements were also made at STXM 11.0.2 at the Advanced Light Source, which is supported by the Division of Basic Energy Sciences of the U.S. Department of Energy.

BI-ThP6 A Novel Technique for the Determination of Orientational Effects in Bio-Composite Materials*, D. Ziskind, T. Geron, S. Fleischer, K. Zhang, **S.R. Cohen**, H.D. Wagner*, Weizmann Institute of Science, Israel

Dentin is a natural composite material consisting of highly mineralized tubules (peritubular dentin, PTD) embedded in an intertubular matrix (ITD) consisting predominantly of collagen. Although the mechanics of dentin has been studied for over a century, only recently has the advent of nanomechanical testing allowed investigation of its microscopic characteristics. In particular, the role of the PTD in overall dentin mechanics can now be explored. By selecting small enough volumes of dentin, the orientational effect of the tubules can be examined. In this study, micron-sized pillars were fashioned by a novel femtosecond laser ablation technique, which avoids the material damage induced when milling is performed by a high energy ion beam or ablation by slower laser pulses. Testing of these structures was performed in a nanoindenter by recording force vs. deformation curves under constant strain rate (until failure) while compressing the pillar with a flat punch tip. These data provided both the modulus and strength of the sample. The small size of the pillars, approximately 20 x 20 microns in cross-section and 100 microns height, guarantee that the tubular orientation is well-defined within a single pillar compression experiment. A statistical correlation was observed between the tubule orientation and measured modulus, with a higher modulus being recorded when the tubule axis was oriented along or near the axis of compression. Such studies allow correlations between the local tubular orientation and biomechanical function. The new method described in this work does not expose the sample to dehydration in vacuum or high energy ions, and does not require coating with conductive materials. It is generally applicable to a variety of biological specimens.

BI-ThP8 Characterizing the Carbohydrate Microarray: XPS, ToF-SIMS, SPR, and ELLA Analysis of Glycan-Modified Surfaces*, **F. Cheng**, M. Dubey, H. Nguyen, S. Jing, J. Burk-Rafel,* University of Washington*, M. Dhayal,* Centre for Cellular and Molecular Biology, India*, D. Ratner*, University of Washington

Self-assembled Monolayers (SAMs), especially alkanethiols on gold, have been extensively used as model system for studying surface modification strategies. In this work, we utilize this platform to fabricate carbohydrate-modified biosensors composed of mixed monolayers of mannose headgroups and oligo(ethylene glycol) (OEG) moieties on gold. We have extensively used x-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), surface plasmon resonance (SPR), and enzyme-linked lectin assay (ELLA) to understand the composition, structure and reactivity of these mixed SAMs to carbohydrate-binding proteins (lectins). XPS and ToF-SIMS results give a clear indication that the composition of mannose on the surface is directly proportional to its molar ratio in solution. However, when these sensors are exposed to lectins, XPS shows that the amount of protein is inversely proportional to the amount of mannose present on the surface. We performed SPR studies to obtain a quantitative comparison of the amount and multivalent binding of lectins on these mixed SAMs. Detailed study of this system using XPS, ToF-SIMS, SPR and ELLA suggests that an optimum density of mannose on the surface is required to improve the sensitivity and stability of these sensors.

BI-ThP9 Interferometric Lithography of Self-Assembled Monolayers*, **J. Adams**, G. Tizazu,* University of Sheffield, UK*, S.R.J. Brueck,* University of New Mexico*, G.J. Leggett,* University of Sheffield, UK*, G.P. Lopez*, University of New Mexico

Self-assembled monolayers (SAMs) have proved to be highly versatile systems for molecular patterning. Previous work using near-field optical methods has demonstrated that exceptional spatial resolution may be achieved using SAM resists, by exploiting the fact that the photosensitive group is confined to a monomolecular film adsorbed to a solid surface. However, near-field methods are serial in nature. Here we have exploited interferometric approaches in combination with SAM resists to fabricate a variety of nanostructured materials. Extremely high resolution has been achieved by exploiting the monolayer nature of the resist. Interferometric lithography (IL) is rapid, and uses minimal instrumentation. IL using a cw, 244 nm frequency doubled Ar-ion laser source has been found to yield structures as small as 35 nm using SAM resists, over macroscopically extended areas. SAMs of alkanethiols on gold may be photo-oxidized to yield weakly bound sulfonates that may be displaced by solution-phase adsorbates to yield patterns of chemical composition. Here, we demonstrate the fabrication of patterns of surface free energy with a period of 200 nm. Protein adsorption may be controlled by using IL to selectively photodegrade oligo(ethylene oxide) (OEG) terminated SAMs of alkanethiols on gold and of trichlorosiloxanes on glass. Nanopatterned streptavidin formed this way retains its ability to bind biotinylated proteins. Finally, monolayers of phosphonic acids on titanium dioxide may be readily patterned and used as templates for the fabrication of a variety of architectures, including 35 nm TiO2 structures on glass. IL is an inexpensive, fast and convenient means of producing molecular nanostructures over square centimetre and larger areas.

BI-ThP10 Absolute Quantification of Bio-molecules Immobilized on Self-Assembled Monolayers, ***H. Min***, *Y.J. Lee, D.W. Moon, T.G. Lee*, KRISS, Rep. of Korea

Biochips such as DNA and protein chips are becoming increasingly important in molecular diagnostics due to their low cost and the need for automated and easy-to-handle techniques. However, only a fraction of biochip products are approved by the FDA for clinical purposes because of the demand for accurate and reproducible biochip performance that can also be quantified. In this study, we develop a new method for the absolute quantification of the probe molecules (DNA, PNA and protein) immobilized on self-assembled monolayers (SAMs) by using medium energy ion scattering (MEIS) spectroscopy. In addition, measuring the amounts of target molecules in interaction with probe molecules on biochip surfaces, we determined the hybridization efficiencies of the DNA-DNA and PNA-DNA systems or the interaction efficiency of the protein-protein system. Our results show that this new methodology would be very useful for quality control of biochips in bio-medical applications.

BI-ThP11 Optically Responsive Nanoparticle Layers for the Label-Free Readout of High-Density Peptide Libraries, ***R. Dahint***, *F.C. Liu, N. Waly, H.O. Guvenc,* University of Heidelberg, Germany, *T. Felgenhauer, F. Breitling,* German Cancer Research Center, Germany, *M. Himmelhaus*, University of Heidelberg, Germany

Recently, we developed a novel complex material with combined optical and biological functionality [1, 2]. It consists of dielectric nanoparticles, which are adsorbed onto a plain gold surface and subsequently metallized by deposition of gold colloid prior to electroless plating. Upon reflection of white light, the layers exhibit pronounced extinction peaks which shift to higher wavelengths when molecules adsorb onto the surface. For simple alkanethiols a significantly higher red-shift of the extinction maximum was observed than reported for conventional surface plasmon resonance. To detect biomolecular interactions in array format it is crucial to guarantee homogenous optical response of the nanoparticle layers on macroscopic scales. We will, therefore, discuss the impact of different coating procedures on the optical properties of the films. To optimize sensitivity, effects of particle layer density, dielectric interlayers and plating time have been investigated. We also compared the response of core-shell nanoparticle layers to the optical properties of surface adsorbed gold colloid films. The final goal is to incorporate high-density peptide arrays into the optically responsive nanoparticle films by combinatorial laser printer synthesis [3] to facilitate label-free high-throughput screening of biomolecular interactions for biomedical and pharmaceutical applications. For this purpose, the peptide probes are embedded into a protein resistant matrix based on poly(ethylene glycol)methacrylate (PEGMA). The stability of both nanoparticle layers and PEGMA coating has been optimized with respect to the chemical and physical requirements of the biomolecular coupling reactions.

[1] R. Dahint, E. Trileva, H. Acunman, U. Konrad, M. Zimmer, V. Stadler, M. Himmelhaus, Biosens. Bioelectron., 22, 3174-3181 (2007)

[2] P. Buecker, E. Trileva, M. Himmelhaus, R. Dahint, Langmuir, 24, 8229-8239 (2008)

[3] V. Stadler, T. Felgenhauer, M. Beyer, S. Fernandez, K. Leibe, S. Güttler, M. Gröning, K. König, G. Torralba, M. Hausmann, V. Lindenstruth, A. Nesterov, I. Block, R. Pipkorn, A. Poustka, F. R. Bischoff, F. Breitling, Angew. Chem. Int. Ed ., 47, 7132-7135 (2008)

BI-ThP12 Enzymatic DNA Polymerization: Potential as Signal Amplification, ***V. Tjong***, Duke Univerisity, *A. Hucknall,* Duke Univesity, *H. Yu, A. Chilkoti*, Duke University

We have developed a new technique for on-chip, isothermal signal amplification using terminal deoxynucleotidyl transferase (TdT), a template-independent DNA polymerase that catalyzes the sequential addition of deoxynucleotides (dNTPs) at the 3'-OH group of an oligonucleotide primer. We utilized TdT's ability to incorporate non-natural fluorescent dNTPs into a long polymer chain of single stranded DNA (ssDNA). We quantified the TdT mediated signal amplification on the surface by immobilizing ssDNA oligomers on a glass surface followed by surface initiated enzymatic polymerization of DNA. We examined the effect of the concentration of the different natural dNTPs, and the molar ratio of fluorescent dNTPs to natural dNTPs on the length of the polymerized DNA strand and the degree of fluorophore incorporation. These experiments allowed us to optimize the polymerization conditions to incorporate a large number of fluorescent nucleotides (up to ~100 fluorescent dNTP/chain) into the ssDNA chain catalyzed by TdT. For Cy3-labeled dATP, this translated to a maximum of ~40 fold signal amplification through the incorporation of multiple fluorophores into the extended DNA chain. This methodology has the attractive attributes that it is both isothermal and on-chip –as the fluorophores are covalently incorporated into a ssDNA chain that is grown from a tethered DNA strand at 37 ºC. We anticipate the use of this amplification modality for the development of sandwich fluoro-immunoassays and DNA microarrays where binding of the detection Ab in a sandwich assay or the target strand in a DNA microarray provides the 3'-OH groups necessary to initiate on-chip fluorescence amplification of the binding event.

BI-ThP13 Surface Characterization of Reactive Surface Patterns and Their Selective Bio-immobilization Reactions, ***F. Liu***, University of Utah, *M. Dubey,* University of Washington, *K. Emoto,* Accelr8 Technology Corporation, *H. Takahashi, D.W. Grainger,* University of Utah, *D.G. Castner*, University of Washington

Surface patterning is often used to immobilize bioactive molecules including proteins, oligonucleotides and small ligands, to localize surface reactions for bioassays and to provide desired cell and bacterial adhesion. This study reports extensive surface analysis of a commercial PEG-based surface chemistry with active ester (NHS)-activity in patterned films. The study followed sequential immobilization and masking reactions on photolithographic patterns used to immobilize peptides, proteins, and cultured cells to specific patterned regions of NHS-reactive or de-activated chemistry.[1] Biotin and peptide patterns were correlated to patterned reactive NHS surface chemistry using high-resolution time-of-flight secondary ion mass spectrometry (ToF-SIMS) for each species. Cell growth and patterning in 15-day serum cultures followed peptide patterns. In other patterned samples, mixed protein (streptavidin and HaloTag™) solutions produced spontaneous self-recognized, bound patterns on photolithographically surface-patterned affinity ligands for each (i.e., biotin and chloroalkane, respectively). The approach uses high-affinity protein-surface self-selection onto patterned PEG-NHS surfaces that exhibit intrinsically low non-specific adsorption background. Fluorescence images and ToF-SIMs imaging of the resulting protein surface selection from mixtures support highly specific interactions of proteins with their respective ligands patterned on the surface.[2] On-going work comparing ToF-SIMs imaging of antibody F_c and F_{ab} fragments supports some ability to produce different whole antibody orientations on neighboring patterns spontaneously. Use of principal component analysis (PCA) helps to increase the ToF-SIMS image contrast and provide protein orientational details based on amino acid compositions.[3]

References:

[1] Takahashi, H., Emoto, K., Dubey, M., Castner, D. G., Grainger, D. W., *Adv. Func. Matls.* 2008. **18**(14): p.2079-2088.

[2] Dubey M., Emoto K., Takahashi H., Castner D.G., Grainger, D.W., submitted, 2009.

[3] Dubey, M., Takahashi, H., Lew, F., Emoto, K., Castner, D.G., Grainger, D.W., submitted, 2009.

BI-ThP14 Temperature-Induced Conformational Changes of Antifreeze Proteins in Aqueous Solution via Overlayer-Enhanced Attentuated Total Reflectance Fourier Transform Infrared Spectroscopy (OE-ATR-FTIR), ***T. Ng***, *D.P. Land,* University of California, Davis, *X. Wen*, California State University, Los Angeles

Protein structural studies are commonly performed using techniques such as X-ray diffraction and Nuclear Magnetic Resonance (NMR). Unfortunately, these techniques make it difficult to study proteins in their native environment. Studies on protein structures via FTIR are often done with high protein concentration or in deuterated solvent. Tethering a protein near the interface of a gold-coated germanium internal reflection element (IRE) concentrates the protein near the interface and allows one to detect the protein with an increased signal-to-noise. By analyzing the amide I spectral region of the protein, the secondary structure of the protein can be determined and any conformational changes in these structures can be monitored. The secondary structure of an antifreeze protein extracted from *Dendroides canadensis* is determined in the aqueous and frozen states and show a decrease in the amount of beta sheet structures and an increase in the amount of turn structures upon freezing.

BI-ThP15 Development of Electric-Field Nanolithography for Selective Surface Modification of Non Bio-Fouling Surface Coatings*, **R. Ferris***, Duke University

Though surface coatings of Poly-Ethylene Glycol (PEG) has been recognised for decades as a particularly effective non-fouling surface, recent advances in polymer brush fabricated thin film Poly-Oligio(Ethylene Glycol) Methyl Methacrylate (POEGMA) has presented a myriad of novel applications. The capability to easily tune brush height and still maintain a high surface grafting density has been shown to prepare surfaces which essentially eliminate the non-specific adsorption of both proteins and cells. Here we present the effects of selectively modifying the surface of polymer brush surfaces, such as POEGMA, via Electric Field Nanolithography (EFN).

EFN, utilizing a spatially localized potential bias to produce chemical modifications sites on a wide range of surfaces, has proven capable of serially modifying the chemical and conformational structure of a variety of polymer-brush film surfaces such as POEGMA, PolyAcrylic Acid, and PolyMethyl Methacrylate surfaces. Such work, however, has presented an interesting and novel bias voltage dependence previously unreported in literature.

Traditionally, EFN has been utilized to produce oxide-rich regions available for further reaction sites processing. Integration of a responsive, non-fouling, polymer brush surface, however, severely alters the voltage modification dependence from the traditional negative tip bias requirement to the now positive tip bias dependence.

Each polymer thin film studied presents a different surface energy landscape, hydrodynamic interaction characteristic, and intramolecular interaction. Presented results, in addition to the contrasted effects seen on spun-coated polymer thin films, will further illuminate the mechanism and effects of EFN integration with polymer brush thin films. In addition to topographical and chemical effects of these thin films, an elevated, film-thickness dependent, threshold bias voltage is reported. Films have been characterized using Xray Photonelectron Spectroscopy, Atomic Force Microscopy, and Contact angle measurements.

In furthering the understanding of how EFN interacts with polymer thin films, it will become possible to produce selective deposition of biological arrays and assays for next generation sensing applications.

BI-ThP16 Template-stripped PZT Thin Films as Substrates for Charge Assisted Assembly of Biological and Organic Molecules*, **R.E. Ducker**, R.T. Hill, A. Chilkoti, B.B. Yellen, S. Zauscher*, Duke University

Ferroelectric thin films, such as Lead zirconium titanate (PZT) have attracted a great deal of interest in recent years due to their piezoelectric and ferroelectric properties. The applications for these films are typically in microelectromechanical systems (MEMS) and ferroelectric non-volatile random access memories. Recently a technique called ferroelectric lithography (FL) has been developed, which can be used to make charged features on surfaces of ferroelectric materials. FL is used to create polarization patterns by applying a voltage to the surface of a ferroelectric material (such as PZT) via an atomic force microscopy (AFM). To achieve this, a DC voltage is applied between the tip and a Pt electrode on the bottom of the PZT to achieve features ranging from 100s of nanometers to several microns. The characterization of the polarization features is done using scanning Kelvin probe microscopy (SKPM). This technique can confirm the presence of an out-of-plane polarization component due to the reorientation of the ferroelectric domains in the PZT. The polarized domains can then be used to direct the assembly of charged entities. To date only inorganic species and gas phase organic molecules has been reported. Here we show the assembly of biological and organic molecules from the liquid phase.

To fabricate these structures an improved method of fabricating PZT thin films with a low roughness is presented. Sol-gel deposition is a relatively cheap and easy method of preparing thin films of PZT. However, films produced in this way can exhibit very high roughness which can make them incompatible with studies involving AFM. We use a template-stripping method to produce extremely flat PZT surfaces. These flat surfaces used in-conjunction with the FL (as described above), can be used to study the directed assembly of charged species on the surface of the PZT using standard AFM techniques. To demonstrate this, the directed assembly of polyelectrolyte layers and proteins on the surface of the PZT is shown.

BI-ThP17 Nano-Dispersion of Ferulic Acid*, **A.S. Madani**, F. Pourmorad*, Pharmaceutical Research Center, Iran

Using natural compounds such as flavonoids in various diseases are under special consideration. Unfortunately poor solubility of flavonoids is an important limitation in preparing pharmaceutical dosage forms. It is reported that preparing nonoparticles can overcome poor solubility problem of the mentioned compounds. The O/ W nano dispersions are a group of preparations in which the poorly soluble drugs could be dissolved in the oil core and/or adsorbed on the O/W interface. Dispersion of flavonoids was prepared by solvent diffusion method in organic phase and lecithine. After adding the dispersion to the aqueous phase, ultrasonication and ultra centrifugation were carried out. A mixture of tween 80 and water were added to the mixture and then ultrasonicated again. Solvent was removed under reduced pressure at 50° C using nitrogen-purged vials. The particles were then evaluated for size and size distribution, zeta potential (ZEN 3000, Malvern, England), shape, percent entrapment, and in vitro release. Differential scanning calorimetry method was used to understand the thermotropic properties and phase transition behavior. Droplet size of nanoparticles of ferulic acid was 108 ± 12 nm.

BI-ThP18 Probing Orientation of Immobilized Humanized Anti-Lysozyme Variable Fragment by Time-of-Flight Secondary Ion Mass Spectrometry*, **J.E. Baio**, F. Chen, L.J. Gamble, D.G. Castner*, University of Washington

The ability to orient proteins on surfaces to control exposure of their biologically active sites benefits a wide range of applications including protein microarrays, antibody-based diagnostics, affinity chromatography, and biomaterials that present ligands to bind cell receptors. As methods to orient proteins are developed, techniques must also be developed that provide an accurate characterization of immobilized protein orientation. In this study, x-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) were used to probe the orientation of a surface immobilized variant of humanized anti-lysozyme variable fragment (HuLys Fv, 26kDa). This protein contained both a His-tag and a cysteine residue, introduced at opposite ends of the HuLys Fv. Previously, we have shown that we could successful control orientation of a Protein G fragment via a cysteine-maleimide bond. To induce opposite end-on orientations of the HuLys Fv variant, it was immobilized onto maleimide oligo(ethylene glycol) (MEG) and nitrilotriacetic acid (NTA) terminated substrates. The thiol group on the cysteine residue will selectively bind to the MEG groups, while the His-tag will selectively bind to the Ni loaded NTA groups. Protein coverage, on both surfaces, was monitored by the change in the atomic % of N, as observed by XPS. The height of the immobilized protein (3nm) was larger than the typical sampling depth of ToF-SIMS, consequently it only samples the top portion of the protein. This was confirmed by principal component analysis (PCA) of the ToF-SIMS results, which demonstrated a clear separation between the two samples based on the intensity differences of secondary ions stemming from amino acids located asymmetrically in HuLys Fv (Histidine: 81, 82, and 110 m/z; Phenylalanine: 120 and 131 m/z). For a more quantitative examination of orientation, we developed a ratio comparing the sum of the intensities of secondary ions stemming from the histidine and phenylalanine residues at either end of the protein. The three-fold increase in this ratio, observed between the MEG and NTA substrates, indicated opposite orientations of the HuLys Fv fragment on the two different surfaces.

BI-ThP19 Biomimetic Metallic Electrodes for Intracellular Electrical Measurements*, **P. Verma**, N. Melosh*, Stanford University

Interfacing living matter to electronics with the ability to monitor and deliver spatio-temporal signals to cells or cell networks is promising for various fundamental biophysical studies and also for applications such as high resolution neural prosthetics, on-chip electrically addressed artificial neural networks and arrayed on chip patch-clamps. Developing an inorganic nanostructure that can specifically and non-destructively incorporate into biological membranes is the key to such an interface. We report an approach towards this interface by functionalizing a nanoscale metallic post to mimic a transmembrane protein to directly insert into the lipid membrane and form a tight seal. These post-electrodes were formed by evaporation and lift-off onto conductive bottom electrodes, with 5-10 nm thick hydrophobic bands around the edge of the post formed by molecular self assembly. We recently reported AFM measurements of these posts inserting into lipid bilayers and showed that different molecular functionalizations adhered within the hydrophobic lipid core with different strengths depending on their molecular mobility. Here we describe nanoscale electrical measurements with these post-electrodes on red blood cells to determine the leakage current at the electrode-membrane interface.

BI-ThP20 An Alternative Solution Based Approach to PTCDI-Melamine Network Fabrication on Au(111)*, **V. Korolkov**, N. Haggerty, M. Blunt, S. Allen, C.J. Roberts, S.J.B. Tendler*, University of Nottingham, UK

Two dimensional (2D)-controlled adsorption is a versatile tool for creating well-defined arrays of biological molecules on surfaces. Such surfaces hold potential for a wide range of future applications, including for the development of biosensors and biomolecular screening technologies. Functionalizing a surface with some periodical structure (or a network) is one promising way to spatially control the adsorption process. Hydrogen-bonded networks are reported to be well-ordered structures, presenting periodical 2D-pores suitable for the adsorption of different guest molecules, and thus may provide a reasonable template for 2D-controlled biomolecular adsorption.

Up to the present, only a few studies have focused on solution based approaches to the fabrication of H-bonded networks, and so in this study we have concentrated our efforts towards optimizing a solution based preparation procedure for perylene tetracarboxylic diimide (PTCDI)-melamine network from dimethylsulfoxide solution. Investigations of the stability of this network over different parameters, led us to a useful, reproducible technique for creation of PTCDI-melamine network over a large surface area. It was shown that temperature plays a crucial role in ordering of PTCDI and melamine molecules on the surface.

Optimal conditions for oligonucleotide adsorption into the network-pores were also determined. This work employed several complementary surface analytical techniques to image the network structure (STM, AFM) and the controlled deposition of biomolecules (AFM, XPS).

BioMEMS Focus Topic
Room: Hall 3 - Session BM-ThP

BioMEMS Poster Session

BM-ThP1 A Novel Nanoporous Carbon Materials for Adsorption Gibberellins Acid from Solution*, J. Li,* Hunan University, PR China and University of Florida*, J.-T. Xia, J.-H. Zhang,* Hunan University, PR China*, **T. Liang***, University of Florida

Gibberellin acid (GA) is one kind of ubiquitous phytohormones that regulates various developmental processes of the plant growth. Monitoring and controlling the phytohormone is very important to ensure the efficient growth of crops to bring a high yield and quality production in agriculture or horticulture. Since the content of phytohormone in a plant is very low, and easily decomposed by heat, light, and oxygen, it is of considerable interest to the phytohormone research to prepare some specific absorbants for adsorption of phytohormone molecules from the solution. A novel nanoporous carbon with tailored pore structure has been synthesized by dynamic carbonization with silica gel networks as a template, which was formed in sol-gel polycondensation using tetraethoxy silane (TEOS) as a silica precursor and sucrose as a carbon source. The pore structures of this kind of nanoporous carbon can be tunable to a high pore volume of 1.25 cm3/g and a large specific surface of 1744 m2/g, providing an high adsorption capacity about 6.8mg/g to the gibberellin acid (GA) in a solution within 9 h reaction time, and which is over 4~5 times higher than the adsorption of protein and starch in the same solution. It is indicated this nanoporous carbon materials has potential application as a novel absorbant in the separation and purification of GA from the solution for its monitoring assay.

Key words: Nanoporous carbon; Adsorption; Gibberellin acid;

Acknowledgments

This work was supported by the National Natural Science Foundation of China (Grants:50772034)

BM-ThP2 Boundary Slip and Nanobubble Study in Micro/Nanofluidics with Atomic Force Microscope*, **Y. Wang**, B. Bhushan*, The Ohio State University

The boundary condition at the liquid-solid interface in micro/nano scale is an important issue in micro/nanofluidics systems. Recent studies have shown that the fluid velocity near solid surfaces is not equal to the velocity of the solid surface on hydrophobic surfaces, which is called boundary slip. The degree of boundary slip is evaluated by a slip length. Theoretical and experimental studies suggest that at the solid-liquid interface, the presence of nanobubbles is responsible for the breakdown of the no-slip condition. Nanobubbles are long lasting on hydrophobic surfaces, and movement and coalescence of nanobubbles are observed with higher scan loads during imaging with tapping mode AFM.

The slip length can be measured with both contact atomic force microscopy (AFM) and dynamic AFM methods. In the contact AFM method, the slip length is obtained by fitting the measured hydrodynamic force applied to a sphere as a function of separation distance between the sphere and solid surfaces when the sphere approaches the surfaces. In the dynamic AFM method, the amplitude and phase shift data of an oscillating sphere are recorded during approach to sample surfaces at low velocities. These data are then used to get the hydrodynamic damping coefficient to obtain the slip length. Until now, slip length has generally been studied on hydrophobic surfaces with AFM. The boundary slip properties of superhydrophobic surfaces are seldom studied. The impact of surface roughness on the obtained slip lengths also needs to be eliminated for superhydrophobic surfaces. Moreover, because the sphere should disturb the nanobubble during approach to sample surfaces in both the contact and dynamic AFM method, a new technique is needed to evaluate boundary slip. Regarding nanobubbles, the current studies mainly focus on their physical properties. The interaction between nanobubbles and the surfaces supporting them is seldom studied. More importantly, the relationship between nanobubble immobility and surface properties should be studied.

In this study, both contact and dynamic AFM methods have been applied to study the boundary slip on hydrophilic, hydrophobic, and superhydrophobic surfaces. A new AFM based technique is proposed to study boundary slip. Nanobubble movement and coalescence, as well as tip-bubble interaction, are studied in detail. The physical interaction between nanobubbles and the surfaces supporting them is investigated. Moreover, the relationship between nanobubble immobility and surface properties of hydrophobic surface is revealed.

BM-ThP3 Surface Plasmon Resonance Imaging of Carbohydrate Microarray: Kinetics, Surface and Solution Binding Affinity*, **A. Tyagi**, M. Yan*, Portland State University

Oligosaccharides are increasingly being recognized as important partners in glycan-lectin binding and cellular signaling. Surface plasmon resonance (SPR) is a powerful tool for the real-time study of the specific interactions between biological molecules. We have developed an efficient surface coupling chemistry to probe carbohydrate-lectin interactions in an array format using SPR imaging. The coupling agent, a thiol-functionalized perfluorophenyl azide, PFPA-MUTEG, allows the covalent attachment of carbohydrates to gold surface by way of CH insertion reactions. The SPR chips were modified with mixed SAMs of PFPA-MUTEG and MDEG before the carbohydrate ligands were arrayed and immobilized. The carbohydrate array was composed of α-1,3-α-1,6-D -mannotriose, α-1,2-D -mannobiose, D -mannose, D -glucose and D -galactose, and the binding studies were carried out using Concanavalin A, a plant lectin that exhibits mannose-binding properties. The kinetic equilibrium constant (KA), adsorption coefficient (KADS) and solution equilibrium constant (KD) were obtained for each carbohydrate at different mixed SAM composition. The SAM containing 10% MDEG showed the highest sensitivity and the least non-specific adsorption. The KADS values for mannotriose, mannobiose and mannose were measured to be 10.3 ± 1.1 x 106, 7.6 ± 1.0 x 106, 1.3 ± 1.0 x 106M-1, respectively.

BM-ThP4 Chemical and Morphological Properties of Amino-Silane Coated Surfaces for DNA Purification*, L. Marocchi, L. Lunelli, L. Pasquardini, C. Potrich, L.E. Vanzetti,* FBK-CMM, Italy*, G. Guella,* University of Trento, Italy*, C. Pederzolli,* FBK-CMM, Italy*, **M. Anderle***, Provincia Autonoma di Trento, Italy

DNA purification and PCR amplification are a requirement for most genetic analysis. Combining these processes in a single micro device minimizes sample loss and contamination problems as well and reduces time and costs of analysis. Different strategies are available to perform DNA extraction on a chip. Here we exploited amino-coated silicon and pyrex surfaces as a tool for specific binding of DNA through the electrostatic interaction between amino groups and nucleic acids. Amino groups have been introduced on the surfaces via silanization carried out in wet condition [1] using three silanes carrying a different number of amino groups and different alkoxy groups ((3-Aminopropyl)triethoxysilane (APTES), (3-Aminopropyl)trimethoxysilane (APTMS) and (3-[2-(2-Aminoethylamino)ethylamino]propyl-trimethoxysilane (AEEA)). The influence of different silanization conditions on surface properties, such as homogeneity and thickness of the silane layer, was also studied by changing solvents, concentration of silane solution and reaction temperature. The kinetic of hydrolysis of the alkoxy groups followed by oligomerization of aminosilanes was characterized by NMR measurements. Amino-coated surfaces were characterized by AFM, XPS and absorption spectroscopy to define their chemical and morphological properties. Multi-amino silane were found less prone to form uniform and tiny layers than mono-amino silanes, resulting less suitable for successive PCR amplification.

Finally, we analyzed the ability of treated surfaces to selectively adsorb/desorb genomic DNA with the aim to purify DNA from unwanted cellular components. Preliminary results suggest this strategy as very promising, permitting to obtain a considerable yield of purified DNA in short time.

[1] Fiorilli, S.; Rivolo, P.; Descrovi, E.; Ricciardi, C.; Pasquardini, L.; Lunelli, L.; Vanzetti, L.; Pederzolli, C.; Onida, B. & Garrone, E. (2008), *Journal of Colloid and Interface Science* **321**, 235-241.

Magnetic Interfaces and Nanostructures
Room: Hall 3 - Session MI-ThP

Magnetic Interfaces and Nanostructures Poster Session

MI-ThP1 Characterization of Aluminum Oxide Tunnel Barrier for use in a Non-Local Spin Detection Device, ***J.R. Abel**, J.J. Garramone, E. Bersch, A.C Diebold, V.P. LaBella*, University at Albany

Aluminum oxide can be utilized as an interface layer between ferromagnetic metals and silicon to achieve spin injection into silicon. Utilizing the spin of the electron as well as its charge has the potential to be utilized for logic devices in the post CMOS era. The goal of our research is to inject and readout spins using a non-local measurement device that utilizes 1-2 nm aluminum oxide interface layers as tunnel barriers.

The first step of fabricating a non-local measurement device out of silicon is the growth of an aluminum oxide tunnel barrier[1]. Si (001) wafers were dipped in 49% HF solution for approximately 2 min to remove the native oxide layer. The wafers were then immediately loaded into an ultrahigh vacuum MBE machine, degassed at 400 C and cooled to room temperature. After cooling, a desired thickness of aluminum was deposited from a Knudsen cell. The sample was then transferred back into the load lock and exposed to approximately 130 mTorr of pure O_2 for 20 min. The process was repeated to create samples with a thickness of 1 nm, 2 nm, and 3 nm of aluminum oxide. Each thickness was grown in 0.5 nm and 1 nm steps. In addition, a 2 nm sample was grown, in one 2 nm step.

X-ray photoelectron spectroscopy was performed to characterize the film stoichiometry. It was observed that all the aluminum was bonded to the oxygen for the films grown in 0.5 nm and 1 nm steps. Whereas the 2 nm sample grown in one 2 nm step not all the aluminum bonded to oxygen, leaving a partially un-oxidized aluminum film. In addition XPS was used to measure the band gap of the fully oxidized films to be 6.61 eV in good agreement with films of similar thickness[2]. We will also report on current voltage measurements of these films after they have been capped with metal and application of "Rowell criteria" to demonstrate tunneling as the dominant transport mechanism.

References:

[1] O. van't Erve, A. Hanbicki, M. Holub, C. Li, C. Awo-Affouda, P. Thompson and B. Jonker, Appl. Phys. Lett. **91**, 212109 (2007).

[2] H.Y. Yu, et al., *Appl. Phys. Lett.*, 81:376, 2002

MI-ThP2 Highly Selective Etching of Magnetic Layer using Organic Gases in an Inductively Coupled Plasma Etching System, ***S.K. Kang**, M.H. Jeon, J.Y. Park,* SKKU Advanced Institute of NanoTechnology (SAINT), S. Korea*, B.J. Park, TH. Min, G.Y. Yeom*, Sungkyunkwan University, S. Korea

Magnetic random access memory (MRAM) 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. Dry etching process of magnetic thin films is one of the important issues for the magnetic devices such as magnetic tunneling junctions (MTJs) based MRAM. MTJs which are the basic elements of MRAM can be used as bits for information storage. CoFeB is a well-known soft ferromagnetic material, of particular interest for magnetic tunnel junctions (MTJs) and other devices based on tunneling magneto-resistance (TMR), such as spin-transfer-torque MRAM. One particular example is the CoFeB–MgO–CoFeB system, which has already been integrated in MRAM. In all of these applications, knowledge of and control over the etching properties of CoFeB is crucial. Recently, transferring the pattern by using an Ar^+ ion milling is a commonly used, although the redeposition of back-sputtered etch products on the sidewalls and the low etch rate of this method are main disadvantages. So the other method which has reported about much higher etch rates of >50 Å/s for magnetic multilayer structures using Cl_2/Ar plasmas is proposed. However, the chlorinated etch residues on the sidewalls of the etched features tend to severely corrode the magnetic material. Besides avoiding corrosion, during etching facets form at the sidewalls of the mask due to physical sputtering of the mask material. Therefore, in this work, magnetic material such as CoFeB was etched in an ICP using the gases which can be expected to form volatile metallo-organic compounds. As the gases, carbon monoxide (CO) and ammonia (NH_3) were used as etching gases to form carbonyl volatiles, and the etched features of CoFeB thin films under by Ta masking material were observed with electron microscopy to confirm etched resolution. And the etch conditions such as bias power, gas combination flow, process pressure, and source power were varied to find out and control the properties of magnetic layer during the process.

MI-ThP3 Instrumentation for the Investigation of Switching Field Distribution on Permalloy ($Ni_{81}Fe_{19}$) Nanoscale Structures, ***J. Bates**, C.V. Cojocaru, Y. Miyahara, P. Grutter*, McGill University, Canada

There is an ongoing interest in understanding the switching field distribution (SFD) of nanoscale patterned magnetic elements, which show great potential for novel applications such as magnetic quantum cellular automata [1] or magnetic random access memory [2] architectures. To make these architectures technologically viable, it is essential for patterned magnetic elements, to have a reproducible and controllable magnetic switching mechanism, thus a narrow SFD. Factors that affect the SFD are not known *a priori* and might be of various natures: thermal effects, shape, imperfections in fabrication, microstructure, edge roughness, seed-layer, anisotropy variations and magnetostatic interactions with neighbors etc.

To address these issues we used a combination of atomic/magnetic force microscopy (AFM/MFM) [3] and transmission electron microscopy (TEM) on indexed arrays of permalloy nanoscale structures, sputter-deposited via stenciling on ultra thin silicon nitride membranes. The stencil-masks used during the deposition process features ordered arrays of nano-apertures, prepared by focused ion beam milling. The stenciling process is parallel, resistless, and allows for the direct organization of structures having different aspect ratios (length/width) into any desired architecture.

Permalloy structures were characterized initially by AFM to assess their topography. Then MFM was used in constant height mode in order to obtain magnetic state (domains) and SFD of the structures. Magnetization reversal was studied by applying an *in situ* magnetic field parallel to the sample surface with a pair of rotating NdFeB permanent magnets. Structures with in plane aspect ratios below 4:1(400nm:100nm) revealed a multidomain state thus complex switching behavior, while structures with an aspect ratio above showed a bipolar state and switched coherently. Structures that switched at lower fields were identified as "early" switchers and structures that switched at larger fields were identified as "late" switchers. TEM images of the "early" and "late" switchers have been compared to normal switchers to look for structural variations, which may induce differences in behavior and broaden the SFD.

[1] R. Cowburn et al., NJP 1, 161(1999)

[2] B. D. Terries et al., J. Phys. D: Appl. Phys. 38, R199 (2005)

[3] X. Zhu and P. Grutter, Phys. Rev. B 66, 024423 (2002)

MI-ThP4 Core and Valence Band Photoemission of M[TCNE] Organic-based Magnets, *M.S. Driver, S.Z. Janjua,* University of Missouri - Kansas City*, K.I. Pokhodnya,* North Dakota State University*, **A.N. Caruso***, University of Missouri - Kansas City

A family of organic-based magnets of $M^{II}[TCNE]_x{\bullet}zS$ (M = V, Mn, Fe, Co, Ni; TCNE = tetracyanoethylene; S = CH_2Cl_2) composition exhibit ordering temperatures ranging from 44 (M = Co, Ni) to ~400 K for M = V. The exchange mechanism in this class of magnets is not well understood and changes dramatically with transition metal type. Core and valence band photoemission have been completed, above and below the transition temperature for the above systems and will be presented. The binding energies of the metal and organic core levels, relative to M^{II} and $[TCNE]^{\bullet-}$ will be presented within the context of exchange strength, transition temperature and metal-to-ligand symmetry overlap. The goal of our groups is to provide, through multiple spectroscopies (some pressure dependent), a picture for the binding energy and spin polarization of the occupied/unoccupied electronic structure as well as the exchange mechanism and bonding as the transition metal type is varied in roughly the same physical structure.

MI-ThP5 Electrical Spin injection from Fe into ZnSe, ***A.T. Hanbicki**, G. Kioseoglou, M.A. Holub, O.M.J. van 't Erve, B.T. Jonker*, Naval Research Laboratory

The wide bandgap semiconductor ZnSe is an opto-electronic material with a comparable spin lifetime and small lattice mismatch to GaAs. Novel spintronic devices that incorporate ZnSe/GaAs heterostructures will require the facile transport of spin information across several heterointerfaces including spin injection into the ZnSe. We have electrically injected spin-polarized electrons from a ferromagnetic Fe contact into a ZnSe epilayer grown on a GaAs heterostructure. The injected carriers proceed through 300 nm of ZnSe and recombine in the GaAs emitting light characteristic of the bulk GaAs exciton. We measure spin polarizations in excess of 40% in the GaAs based on analysis of the circular polarization of the electroluminescence. We report results as a function of applied magnetic field, device current and temperature. The spin injection process and transport through the ZnSe layer sustains significant spin populations in this heterostructure.

This work was supported by core programs at NRL.

MEMS and NEMS
Room: Hall 3 - Session MN-ThP

MEMS and NEMS Poster Session

MN-ThP1 Imprinting of Guide Structures to Weave Nylon Fibers, ***H. Mekaru***, *M. Takahashi*, AIST, Japan

We are developing a large-area display and a wearable health checker by weaving fibers with an electrical circuit on their surface. In this technique, a guide structure that determines the position to fix fibers was processed on the fiber by a thermal nanoimprint technology. We used two kinds of molds with guide structures with different cross-sectional shapes (rectangle and arc). Micropoles to connect the fiber were arranged in the bottom side of the guide structures. In the case of guide structure with a rectangular pattern, the multilayer structure was formed on a Si substrate using MEMS technology; and Ni mold was made by electroforming. Fifteen convex rectangles with their length, width, and height as 14.4 mm, 100 µm and 50 µm were arranged in a 1-mm pitch formation. And, 10-µm deep column holes with the diameters of 5, 10, and 20 µm, were fabricated on the upper side of the guide structure. The other kind of guide structure with an arc pattern was processed by precision machining. A 150-µm-thick Ni-P layer was electroless-plated on an Inconel-600 alloy substrate and the layer was then coarse-processed by dicing. The finish processing employed a 20-µm-diameter diamond endmill and a Robonano α-0iB (FANUC Ltd.). Thirteen arc guide structures with 20-µm-diameter holes were processed for 4 hrs. The length, bottom-width, and height of the individual guide structure were 15 mm, 160 µm, and 100 µm. Hemispherical holes with 20 µm diameter and a maximum depth of 10 µm were processed on the upper side of the guide structure. The size of each type of mold was the same 20 mm square. The guide structures from the two kinds of molds were imprinted on a 90-µm-diameter nylon fiber (Amilan, Toray Industries, Inc). In the imprinting experiments, a desktop thermal nanoimprint system NI-273 (Nano Craft Technologies Co.) was used. Molding conditions were: heating temperatures = 100 °C, cooling temperature = 70 °C, loading force = 100 N, and holding time = 1 s. The guide structure and micropoles were successfully transcribed from the mold onto the nylon fiber. The side-view of the guide structure was examined with an optical microscope and the pressed depth was measured as 21 µm, regardless of the kind of mold used. After the imprinting, the weaving of the fiber was carried out with tweezers under an optical microscope. Each guide was confirmed to be connected to each fiber. It was easy to weave the arc guide structure processed with machining because the guide sidewall was curved. In future, weaving of fiber with variety of electric circuit patterns will be presented.

MN-ThP2 Test Instrument for the Tensile Strength of Micro-Nano Materials, ***A. Kasahara***, *H. Suzuki, M. Goto, H. Araki, P. Yuriy, M. Tosa*, NIMS, Japan

There is considerable research at present on the performance and properties of nanosheets, nanofibers and other functional nanomaterials such as fullerenes and nanotubes. This is particularly true of carbon nanotube, made from carbon atoms, where many research projects throughout the world are looking at measurement techniques for evaluating electrical and electronic characteristics with a view to developing electronic device applications such as high-intensity field-emitted electron sources and ultra-fast transistors. However, we have not yet to see a genuine, flexible methodology for evaluating the key characteristic of mechanical strength essential to micro-nano structural materials development — the nanoscale equivalent of tensile strength testers for ordinary materials. This is due to the inherent difficulties associated with the manipulation and transportation of materials at the micro-nano scale level. Here, we will discuss our recent results on mechanical strength measurement of micro-nano wires in diameter several nm through several thousand nm and in length several mm by means of prepared micro-nano tensile strength tester device.

MN-ThP3 Morphology and Mechanical Properties of Block Copolymer Films for Bone Regeneration Applications, *B. Bhushan*, ***M. Palacio***, *S. Schricker*, The Ohio State University

Biocompatible polymers act as scaffolds for the regeneration and growth of bones. In dentistry, these can be used to treat diseases with accompanying bone loss, such as aggressive periodontitis. Surface morphology, specifically the presence of nanostructures, is expected to affect the adhesion of the cells adsorbed on the surface, which should be optimized for successful cell growth. Block copolymers are of interest as scaffold materials because a number of them are biocompatible, and their nanostructure is easily tunable with synthetic techniques. In this investigation, atomic force microscopy (AFM) studies were conducted for two block copolymers, namely, poly(methyl methacrylate-*b*-acrylic acid) and poly(methyl methacrylate-*b*-hydroxyethyl methacrylate). The topography, stiffness, phase angle, and friction maps were obtained in dry and aqueous environments in order to study the morphology, elasticity, viscoelasticity, and friction properties, respectively. Results of AFM imaging identified the presence of polymer domains corresponding to the copolymer components. Images taken in an aqueous medium reveal greater contrast as a consequence of the differential water absorption between the copolymer components.

MN-ThP4 Mechanically Durable Superhydrophobic, Self-Cleaning, and Low-Drag Surfaces with Hierarchical Structure, ***Y.C. Jung***, *B. Bhushan*, The Ohio State University

Superhydrophobic surfaces exhibit extreme water-repellent properties. These surfaces with high contact angle and low contact angle hysteresis also exhibit a self-cleaning effect and low drag for fluid flow[1-4]. For the development of superhydrophobic surfaces, which is important for various applications such as glass windows and solar panels, alternative materials and fabrication methods need to be explored to improve durability[5]. It is necessary to perform durability studies on these surfaces in order to identify fabrication techniques and materials that can best withstand real world applications. Micro-, nano-, and hierarchical structures which would lead to superhydrophobicity and self-cleaning are prepared using different fabrication methods. In order to compare the durability of the various fabricated surfaces, friction and wear studies are performed at the microscale using a pin-on-disk test, where a stationary pin applies a constant normal load while sliding on the sample surface. Waterfall and waterjet tests are also conducted to determine the loss of superhydrophobicity by changing the flow volume and pressure conditions, respectively. The changes in the surface morphology and structure and the wettability are examined by SEM and AFM imaging and contact angle measurements, respectively .

[1] Bhushan, B., *Nanotribology and Nanomechanics – An Introduction*, 2nd ed., Springer-Verlag, Heidelberg, Germany, 2008.

[2] Bhushan, B., "Biomimetics: Lessons from Nature - An Overview", *Phil. Trans. R. Soc. A* 367, 1445-1486.

[3] Nosonovsky, M. and Bhushan, B., Multiscale Dissipative Mechanisms and Hierarchical Surfaces: Friction, Superhydrophobicity, and Biomimetics, Springer, Heidelberg, Germany, 2008.

[4] Bhushan, B. and Jung, Y. C., "Wetting, Adhesion, and Friction of Superhydrophobic and Hydrophilic Leaves and Fabricated Micro/Nanopatterned Surfaces", *J .Phys: Condens. Matter*. 20, 225010 (2008).[5] Bhushan, B. Jung, Y. C. and Koch, K., "Micro-, Nano-, and Hierarchical Structures for Superhydrophobicity, Self-Cleaning and Low Adhesion", *Phil. Trans. R. Soc. A* 367, 1631-1672 (2009).

MN-ThP5 Tripod Honeycomb Shape Scaffold for Retina Cell Culture by Dynamic Mode Multidirectional UV Lithography, ***J. Kim***, *J. Yang, M.M. Slaughter, G. Kim, Y.-K. Yoon*, University at Buffalo, the State University of New York

Since the cytoskeletal properties of the cells cultured in two-dimensional (2D) culturing environment are different from those of the real biological cells constituting three-dimensional (3D) organs, the *in-vitro* cytokinetics from a 2D scaffold cannot be applied to *in-vivo* 3D cell culturing study. In this research, a 3D tripod honeycomb shape scaffold array fabricated using automated dynamic mode multidirectional ultra violet (UV) lithography [1] has been demonstrated for efficient 3D cell culture. A unit element of the scaffold consists of honeycomb shape confinement on the top, three posts at the bottom, and tapered openings in the side walls. **This architecture provides advantageous properties for 3D cell culture: (1) sufficient nutrient supply paths through the openings in the side walls, (2) mechanically stable tripod structure, (3) moldable 3D geometry useful for mass production with various material selection, and (4) structural flexibility amenable to further 3D macro shaping.** SU-8 (negative tone photoresist) mold masters made by multidirectional lithography, replicas with biodegradable polymer (poly lactic-co-glycolic acid: PLGA) after micromolding, and macroscopically deformed scaffolds are successfully demonstrated. As a test vehicle, retinal cells [2] are successfully cultured on the fabricated PLGA scaffold.

Polydimethylsiloxane (PDMS) has been used to make a negative form of the mold master. A broad range of materials can be used for the final polymeric structure. In this research, PLGA has been cast to form a final scaffold.

The structural compliance associated with the tapered sidewall provides macroscopic flexibility, one of the unique merits of this architecture. A rounded scaffold for the potential usage of artificial blood vessels or other implant devices is demonstrated. A unit scaffold layer has a height of 300mm and multilayer scaffolds can be implemented for much thicker 3D cell culturing by stacking multiple layers.

[1] J.K. Kim et al, “Automated dynamic mode multidirectional UV lithography for complex 3-D microstructures,” Proceedings of IEEE Micro Electro Mechanical Systems, Jan. 13-17, 2008, Tucson, AZ, pp. 399 – 402.

[2] X Luo et al, “Susceptibilities to and Mechanisms of Excitotoxic Cell Death of Adult Mouse Inner Retinal Neurons in Dissociated Culture,” Invest Ophthalmol Vis Sci., 45 (2004), pp. 4576–4582.

MN-ThP6 Micro Accelerometer with Mechanically Nonlinear Self-Limited Bistable Suspension*, **E.M. Amir**, S.L. Krylov*, Tel Aviv University, Israel

We report on operational principle, modeling and design of an electrostatically actuated accelerometric device with mechanically nonlinear suspension element. The device incorporates a proof mass actuated by a parallel-plate electrode and attached to a substrate by initially curved beams in such a way that both electrostatic and inertial forces are directed along the beam. In accordance with the exact extensible *elastica* and approximate reduced order models of the beam used for the analysis, the deformation of an initially curved slender beam subjected to an end force can be subdivided into two stages - the "bending" stage associated mainly with the straightening of the beam and the "tension" stage corresponding to elongation of the almost straight beam. Since the stiffness of the beam at the first stage is significantly lower than at the second stage, the force–displacement dependence of this kind of suspension is of self-limiting type and the beam can be viewed, in a sense, as one directional constraint. Application of nonlinear electrostatic force results in electrostatic (pull-in) instability followed by the steep increase in the straightened beam stiffness preventing contact with the electrode and resulting in appearance of an additional stable configuration and bistability of the beam.

In this research we present two operational principles for measuring the acceleration - the pull-in voltage monitoring and the resonance frequency shift monitoring. The pull-in voltage approach is based on the (found to be close to linear) dependence between the pull-in voltage and the acceleration, while the self-limiting characteristic of the suspension prevents undesirable from the reliability point of view contact between the proof mass and the actuation electrode. The resonance frequency approach is based on the monitoring of the resonant frequency shift appearing due to acceleration and significantly enhanced in the vicinity of the pull-in instability points. Model results show that using suggested approach significant improvement, comparing to conventional designs with linear flexures, in the device performance could be achieved and μg resolution combined with extended dynamic range are feasible for relatively simple architecture and well established silicon on insulator (SOI) based fabrication process.

MN-ThP7 Creation of Co-planar Oxide Pillars for Fabricating Overhanging Metal Structures*, **S.A. Hickman**, E.C. VanWerven, J.C. Ong, J.A. Marohn*, Cornell University

Magnetic resonance force microscopy (MRFM) combines the nanoscale resolution of scanned probe microscopy with the three-dimensional, isotopically specific imaging capabilities of magnetic resonance imaging. The ultimate goal of MRFM is to achieve single-proton imaging resolution and create an atomic-resolution three-dimensional image of a individual molecule. At this level, the technique could achieve such feats as the structural determination of a single copy of a protein or macromolecular complex, making it a fantastic tool for biological study.

The key technology for MRFM is extremely sensitive, magnet-tipped cantilevers. While extensive effort has gone into fabricating such cantilevers, thermally-limited cantilever sensitivity is seldom achieved in practice because of surface-induced dissipation. The design of our cantilever minimizes this noise by extending the magnet past the cantilever tip. In our current cantilever fabrication scheme, we deposit the magnet on the device layer of a silicon-on-insulator wafer, and then create an overhanging magnet by using an isotropic sulfur hexafluoride etch to partially remove the silicon under the magnet. While successful, this process raises concerns over possible damage to the magnet from the etch species, and there is some degree of variability in the length of the overhang because of the very high silicon etch rate. To mitigate these issues, we have developed an alternative process in which the magnet is deposited over a pillar of silicon oxide extending through the device silicon layer and conformal with the top of this layer. This innovation removes the plasma etching step of our previous approach, and the length of overhang can be controlled by changing the lithographic placement of the magnet relative to the edge of this pillar. The pillar is created by localized oxidation of the device silicon, followed by chemical mechanical planarization. In this poster we will present our progress on this work, as well as present ideas for uses of our innovation well beyond cantilevers for MRFM.

MN-ThP9 Fabrication of a Vibratory Gyroscope Based on Piezoelectric Actuators and Sensors using MEMS Technology*, **V. Rincon**, H. Nampoori, A.L. Highsmith, S. Kotru*, University of Alabama

Piezoelectric materials are commonly used in micro electro mechanical systems (MEMS) due to the self-generating sensing, large actuation amplitude with low voltage, and compatibility to integrated circuit process. In this work we have used Nb-doped Pb(Zr$_{20}$,Ti$_{80}$)O$_3$ (PZT) films for fabricating actuators and sensors for a micromachined vibratory gyroscope. PZT films exhibit higher values of effective transverse piezoelectric coefficient ($e_{31,f}$) and effective longitudinal piezoelectric coefficient ($d_{33,f}$) compared to any other available piezoelectric materials.

The complete gyroscope device consists of one active wafer, two handler wafers and a Si post bonded together. The active and handle wafers were fabricated using MEMS technology. Entire processing was done in a clean room environment using the state of art micro fabrication facility (MFF) at the University of Alabama . First, PNZT was deposited on both side of the active wafer resulting in PNZT/Pt/TiO$_2$/SiO$_2$/Si/SiO$_2$/TiO$_2$ /Pt/PNZT stack. This step was followed by SiO$_2$/Ti/Au deposition using an e-beam evaporator. Processing the active wafer involves five masks and twenty four photolithography steps. Sine the device is on both sides of the wafers, one side was always protected with photoresist while the other side of the wafer was being processed. The final structures were released by etching away various film layers using a combination of dry and wet etching techniques. This includes three different etching techniques viz., ion mill, oxide etcher, and wet etch.

For the handle wafers Cr films were deposited on Si wafers using an e-beam evaporator. A photo-defineable polyimide was then spun on these wafers and patterned. These patterns were transferred using two masks and two photolithography steps. The active and handle wafers were then bonded together and the Si post attached to it to form the complete device. Details of the fabrication process of the device and its evaluation will be presented.

Plasma Science and Technology
Room: Hall 3 - Session PS-ThP

Plasma Science Poster Session

PS-ThP1 3D Numerical Modeling and Experimental Characterization of Internal Antenna Type Inductively Coupled Plasma System for Nitriding of Bipolar Plates for PEMFC(Polymer Electrolyte Membrane Fuel Cell)*, **J. Joo**, W. Yang*, Kunsan National University, Republic of Korea*, J. Lee*, Seoul National University, Republic of Korea

Bipolar plates for PEMFC(polymer electrolyte membrane fuel cell) are crucial in determining service life of hydrogen fuel cells. The required anti-corrosion characteristics is very hard to meet with commercial materials, e.g. 316 stainless steels while keeping other requirements, e.g. electrical conductivity, mechanical formability and cost. Thin film coatings could be substitute solution but fairly marginal due to its relatively high cost. Second option is surface nitriding using high density plasma sources with appropriate substrate bias. Plasma nitriding at high temperature upto 800°C is a stable technology for automobile parts and tools. Stainless steels do not allow to go over 500°C due to its microstructural phase transformation. Low temperature, high rate nitriding technology is very crucial technique in this field. Bipolar plate is in a thin sheet form of 300 x 300 mm as thin as 0.5 mm. We used internal antenna type inductively coupled plasma as a source of nitriding species. The mixing ratio of nitrogen and hydrogen was varied to give optimal plasma generation condition. Plasma diagnostic techniques, e.g. Langmuir probe measurement, optical emission spectroscopy, and biasing voltage/current waveform measurements were used to characterize the process. For optimal design of industry scale systems, we used a 3D computational fluid dynamic code (CFD-ACE+). Number of antenna turns, relative positions of antenna and loaded sheets, gas pressure and composition were varied and diagnosed experimentally. In addition, substrate biasing schemes were studied. Final anti-corrosion characteristics showed that pulsed dc bias of 50 kHz with 600 W of ICP was giving best corrosion current density among others; 316 stainless steel, Cr, CrN with dc bias.

PS-ThP2 Multidimensional Plasma Simulations of an SF_6/O_2 Etch, *J. Tennyson,* ***S. Harrison****,* University College London, UK*, J.J. Munro, D. Brown*, Quantemol, UK

Sulfur Hexafluoride (SF_6) is the plasma processing gas that is used industry-wide in a range of processes for the dry etching of silicon. However, the performance and efficiency of different processes and machines can vary widely. Through simulation we can gain significant insight into the optimization problem and provide a low cost means for further development.

SF_6 is also very bad for the environment with a Greenhouse Warming Potential that is 22,000 times that of CO_2. Therefore it is vital that SF_6 is used sparingly and efficiently in every process. Here, simulation can help to find ways of remediating harmful waste gases and optimize the process for typical processing goals (e.g. etch rate, uniformity) as well as improving SF_6 consumption efficiency and other environmental measures.

Here we present an full chamber 2D simulation of an SF_6/O_2 silicon etch process, building upon previous calculations of SF_6 plasma chemistries using Quantemol-P [1]. Etch rate, pressure and power trends along with chamber wide contour plots of gas-phase species concentrations and fundamental plasma properties are considered.

To perform these calculations and build this model a new software tool is being constructed and will be demonstrated. The plasma simulation itself is run using a set of algorithms and codes based on HPEM [2]. The new code will integrate with outputs from Quantemol-N [3], which provides data on molecular processes, and Quantemol-P. It will provide

a set of design and specification tools, along with an expert system for running HPEM and a design of experiments (DOE) type calculation system.

[1] J.J. Munro and J. Tennyson, J. Vacuum Sci. Tech. A, 26, 865 (2008)

[2] R.J. Hoekstra, Michael J. Grapperhaus and M.J. Kushner, J. Vacuum Sci. Tech. A, 15, 1913 (1997).

[3] J. Tennyson, D.B. Brown, J.J. Munro, I. Rozum, H.N. Varambhia and N. Vinci, J. Phys. Conf. Series, 86, 012001 (2007).

PS-ThP3 Semi-analytical Model of Standing Wave and Skin Effect in Large-area RF Discharges***, M. Klick***, Plasmetrex, Germany

Large area plasma coating becomes more important with increasing diameter of semiconductor wafers and thin film Si solar cells. The layer characteristics depend on the plasma, the uniformity depends mainly on the plasma sheath voltage at the substrate via the ion energy distribution and the corresponding back-etch rate. Therefore the modeling of large-area CCPs is increasingly important. In particular the skin and standing wave effects must be involved, beside the non-homogeneous distribution of chemically active species in plasma these effects are the major root causes of non-uniform interaction plasma and surrounding solid bodies.

A semi-analytic, cylindrical and 2d plasma model based on the full set of the Maxwellian equations was developed. It involves also the non-uniformity and nonlinearity of the plasma sheath as nonlinear boundary condition. It involves dynamic electron effects by a fluid model for the plasma bulk and nonlinear mechanisms by a nonlinear sheath model.

The model includes nonlinear effects and provides so the dependence of the Fourier spectrum of the local RF current on geometry, plasma density, and the electron collision rate. The ratio of the excitation frequency to the resonance frequencies of the spatial mode is found to determine the nonuniformity caused by the standing wave. The collisional skin depth can be also estimated. Thus the mean sheath voltage varying along the grounded electrode through both standing wave and skin effect can be easily calculated and understood by means of a semi-analytical model.

Both a center and edge maxima or even spatial oscillations in the mean sheath voltage at the grounded electrode can be observed. This is in agreement to experimental results of Si deposition used for comparison. It can be also shown that well-known terms as symmetry loose sense for very 'flat' RF discharge systems, they can be symmetric in the center and asymmetric near the edge.

PS-ThP4 U-shaped Internal Inductively Coupled Plasma Source with a Ferrite Module for Roll-to-Roll Processing***, S.P. Hong****, J.H. Lim, K.N. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Flexible display devices are being investigated by many researchers as a potential next-generation display. Roll-to-roll plasma processing is one of the important techniques for flexible display processing. For the fabrication of flexible display devices by the roll-to-roll plasma processing, not only highly uniform plasma processing but also high processing rates are required to increase the throughput of the processing. In particular, for the use of low-temperature substrates such as plastic substrates, the processing at the temperature lower than 100 ℃ is required.

In this work, we present a line-type, high-density plasma source composed of a U-shaped internal antenna for an inductively coupled plasma (ICP) operated at 2 MHz and with a ferrite module installed on the antenna of the ICP source. The 2300 mm long χ 740mm wide ICP source showed the plasma density of about 3.1 χ 10^{11}cm^{-3} at 3.5kW with the plasma uniformity less than 11% along the antenna line. The plasma characteristics of the source were measured using a Langmuir probe (Hiden Analytical Inc., ESP), and the electrical properties of the line-type, internal antenna were measured using an impedance analyzer (MKS Inc.).

PS-ThP5 Self-Consistent Electrodynamics of Very High Frequency Plasma Discharge Chambers***, Z. Chen****, J.A. Kenney, S. Rauf, K. Collins*, Applied Materials, Inc.

Very high frequency (VHF) radio-frequency (RF) sources are used for many plasma processing applications including material etching and thin film deposition. However, when chamber dimensions become commensurate with RF wavelength, electromagnetic effects have a significant influence on plasma behavior. We present a 2/3-dimensional model for self-consistently studying both electrodynamic and plasma dynamic behavior of complete RF plasma discharge chambers. The model is fully self-consistent in the following senses: (1) Maxwell's equations and transport equations for charged and neutral species are coupled and solved explicitly in time domain; (2) The complete RF plasma discharge chamber including the RF power delivery sub-system, electrodes and plasma domain is modeled all together and simultaneously; and (3) The RF source is naturally applied onto the transmission line of the RF feed system in the form of an electromagnetic wave rather than hard imposition of assumed RF sources onto the electrodes or on the boundary of plasma. In the model, Maxwell's equations are discretized using the Finite-Difference Time-Domain (FDTD) method, and plasma discharge is modeled by solving the time-dependent continuity equations for charged and neutral species, drift-diffusion approximation for specie fluxes, and the electron energy conservation equation. Such a systematic approach is equally applicable to both capacitive and inductive discharges. It is useful for understanding not only electrodynamic effects in large-area VHF plasma chambers, but also the impact of asymmetric parts in RF systems and electrodes on the symmetry and uniformity of electric field and plasma in discharge region, which is of significant interest in industrial applications of RF plasma chambers. We first apply the model to study the impact of azimuthally asymmetric dielectric and conducting perturbations in the RF feed system on plasma uniformity. Then we examine the effect of transmission line length and impedance on plasma profile, especially in regimes close to resonance. We also explore the potential application of VHF source in large area (> 5 m^2) capacitively coupled plasmas. Based on the model, we have been able to identify a variety of design approaches for ensuring electric field and plasma symmetry and uniformity in discharge region.

PS-ThP6 Characterization of a Power Splitter for Multi-Tile Plasma Source for VHF/UHF PECVD Film Growth*, A.R. Ellingboe,* Dublin City University, Ireland, ***T. Michna***, Phive Plasma Technologies, Ireland

A novel divide by arbitrary-N power divider for use in the 100-500 MHz frequency range will be introduced. Electrical characterization of the power divider will be reported. The system has been successfully applied to an extensible, multi-tile plasma source operating from below 100 MHz to over 400 MHz. The plasma is found to light uniformly over the electrode surface for electronegative and electropositive gasses; and a 300mm diameter plasma has been sustained at under 15 Watts.

In multi-tile electrode solutions, the plasma load on the power splitter can result in spatial inhomogeneities in plasma creation; this fault is overcome by careful design of the system. A narrow-gap 300mm by 400 mm plasma is found to light uniformly over the electrode surface for electronegative and electropositive gasses at pressures from 10 mTorr to 3 Torr; plasma has been sustained across the full volume at under 25 Watts.

PS-ThP7 Experimental and Numerical Investigations of a Hollow Cathode Plasma Source for Microcrystalline Silicon Deposition***, F.C. Tung****,* ITRI/MSL, Taiwan, R.O.C.*, T.C. Wei,* Chung Yuan University, Taiwan, R.O.C.*, S.W. Chau,* National Taiwan University of Science and Technology, R.O.C.*, P.S. Wu,* ITRI/MSL, Taiwan, R.O.C*, C.-H. Lin*, Chung Yuan University, Taiwan, R.O.C.

Microcrystalline silicon thin films were grown by plasma enhanced chemical vapor deposition from a mixture of silane and hydrogen gases at low temperature. The effect of process parameters on the velocity, temperature and species concentration profiles are reviewed in this article. Several numerical simulation and in-situ plasma diagnostics on a hollow cathode plasma source and a process chamber are compared, which can be used to characterize the plasma properties. A global plasma model is developed for the plasma source and a CFD model is developed for the process chamber. Diagnostics of the plasma are carried out using a

Langmuir probe and optical emission spectroscopy. Based on these investigations, an updated view on the role of the process parameters is presented.

PS-ThP8 Novel Long Linear-Type Microwave Plasma Source, ***C.C. Chang***, Industrial Technology Research Institute, Taiwan

A novel long linear-type microwave plasma source using a variably-reduced-height rectangular wave-guide as the plasma reactor has been developed. Microwave power is fed from the both sides of the wave-guide and is coupled into plasma through a long slot cut on the broad side of the wave-guide. The reduced height of the wave-guide is variable in order to control the coupling between microwave and plasma so that the plasma is able to attain better uniformity when extending the length of the linear-type plasma source.

PS-ThP9 Time Resolved Energy Distributions for Positive Ions in an Inductively-Coupled Plasma Reactor, ***J.A. Rees***, *C.L. Greenwood, D.L. Seymour*, Hiden Analytical, UK

The energy distributions of positive ions created in an inductively–coupled plasma have been examined using a Hiden EQP mass/energy analyzer. Time-averaged distributions were measured with and without the presence of a Faraday shield between the external RF excitation coil and the glass wall of the reactor. With the shield in position, the coupling of power into the plasma was purely inductive, but without it there was a significant capacitive contribution. The time-average distributions were measured both for continuous power applied to the plasma and for the case where the RF supply was pulsed. For this latter series of experiments, time-resolved distributions were also measured, and the decay in the energies of the ions as a function of time in the afterglow of the plasma was examined. The time-resolved data were obtained by gating the operation of the EQP analyzer either at the ion-counting detector of the instrument or, alternatively, by pulsing a grid mounted behind the sampling orifice of the instrument. The measured energy distributions were independent of the gating method. The distributions for the inductively-coupled and inductive/capacitive coupling are compared.

PS-ThP10 Influence of Sheath on Measurement of Electron Density in Frequency Shift Probe and its Application to Measurement of Electron Temperature, ***K. Nakamura***, *Q. Zhang, H. Sugai*, Chubu University, Japan

In advanced materials processing for manufacturing LSI devices, improvement of accuracy and repeatability has been required to achieve high performance plasma processes. In general, temporal variation of plasma components is believed to be one of reasons for the problems, so it is important to develop technologies for accurate plasma control. We have developed a frequency shift probe as a novel in-situ plasma monitoring technology. The probe enables us to measure an electron density from variation of resonance frequency of the probe head, and the density measurement is possible under minimum disturbance to the processing plasma because of its plane structure. Furthermore, the probe is applicable to a reactive plasma such as fluorocarbon plasmas since the deposited polymer has no significant effects on the resonance frequency. When the resonance frequency of the probe varies from f_0 (GHz) to f_r (GHz) by producing the plasma with the electron density of n_e, (10^{10} cm^{-3}), the value of n_e is given by $n_e=(f_r^2-f_0^2)/0.81$. However influences of a sheath formed around the probe have not been considered in the formula. In this work, sheath effects on the frequency shift probe were investigated based on finite difference time domain (FDTD) simulation, and it was examined how much influences on the measured density the sheath has. Furthermore, the frequency shift probe was tried to be applied to measurements of electron temperature using the sheath effects. As the sheath thickness increased, the resonance frequency decreased since effective permittivity of the media around the probe head decreased. Such a decrease of the resonance frequency was observed regardless of the slit width, however its dependence on the sheath width was affected by the slit width, and it became significant as the slit width decreased. The sheath width is proportional to Debye length, so the resonance frequency of the frequency shift probe is a function of electron density n_e and electron temperature T_e. This means that resonance frequencies obtained in two frequency shift probes having different sheath dependence gives an unique solution of n_e and T_e. Actually, in a experiment using a plasma produced with 13.56 MHz RF power up to 400 W at an argon pressure of 3 mTorr, the present method derived 7.5×10^{10} cm^{-3} in n_e and 4.8 eV in T_e which comparatively showed good agreements with values measured by a Langmuir probe.

PS-ThP11 High Performance of Compact Combinatorial Etching Process for Next Generation Plama Nano-Process, ***Ch.S. Moon***, *K. Takeda,* Nagoya University, Japan*, Y. Setsuhara,* Osaka University, Japan*, M. Shiratani,* Kyushu University, Japan*, M. Sekine, M. Hori*, Nagoya University, Japan

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, nano-leveled precise control has been indispensable to achieve the process requirements. However, up to now, it was an obvious fact that a lot of trials-and-error processes have been carried out in the development of plasma etching processes in which were characterized by external parameters (input power, working pressure, mixture gas ratio), since there has never been any scientific principle based on plasma science. We hereby propose the development of process map, Plasma Nano Science in which the process results are characterized by internal parameters (fluxes and energy distributions of ions, radicals, substrate temperature). For the breakthrough of next generation plasma nano-process guided by Plasma Nano Science, we have developed the combinatorial plasma etching process, in which a variety of results could be acquired by one trial. In this work, the compact combinatorial plasma apparatus was realized in inductively coupled H_2/N_2 plasma driven by two low-inductance (LIA) antennas for etching of organic low-k dielectric films. The spatial distributions of H and N radical densities were measured by vacuum ultraviolet absorption spectroscopy (VUVAS) system and RF-compensated Langmuir Probe (Scientific Systems Smart Probe^{TM}) was used to record the spatial distributions of electron densities, temperatures and energy distributions. In this paper, we present high performances of combinatorial etching process. Etching characteristics such as etch rate and profiles were analyzed in terms of internal parameters rather than conventional external parameters by controlling respective LIA antennas independently.

PS-ThP12 Tailoring of Substrate RF Bias Voltage Waveform for Arbitrary Energy Distributions of Bombarding Ions in Plasma Processing: Ion Energy Measurements, ***X.V. Qin***, *Y.-H. Ting, A.E. Wendt*, University of Wisconsin-Madison

In plasma etching of semiconductors for integrated circuit fabrication, positive ions are accelerated by a sheath electric field directed towards the substrate, where, upon impact at normal incidence, they enhance etching to produce anisotropic feature profiles. Varying the amplitude of a sinusoidal bias voltage waveform applied to the substrate electrode may be used to coarsely control the average energy of bombarding ions through its affect on the dc component of the sheath voltage, but the sinusoidal waveform also produces a broad spectrum of ion energies under typical process conditions. A bias voltage waveform with its shape tailored for the purpose of producing ion energy distributions (IED) with one or two groups of ions with a narrow spread around selected energies has been previously utilized to highlight the significant role of the IED in fluorocarbon-based etching. Presented here are direct IED measurements made with an Impedans^{TM} retarding field energy analyzer situated on the biased electrode. Measurements in a 10 mTorr helicon argon plasma in which ion flux and ion energy at the substrate are independently controlled clearly demonstrate the ability to predictably produce arbitrary IEDs at the substrate by tailoring the shape of the bias voltage waveform. Results to be presented for sinusoidal (500 kHz-10 MHz) and tailored (500 kHz) waveforms are compared to predictions based on computation of ion trajectories through the sheath electric field (assumed to instantaneously follow the Child-Langmuir Law), in order to evaluate the accuracy and limitations of this method. For the sinusoidal waveform, the expected broad, bimodal IED is produced, with a reduction in IED width with increasing frequency in agreement with model predictions. Under conditions where the sheath transit time of the ions is short compared to the RF bias period and where ion motion in the sheath is collisionless, tailoring of the waveform produces one or two peaks in the IED, and in the latter case, the energies and relative fluxes of the two peaks can be varied independently through waveform shaping.

*Support from the Lam Research Corporation and the UW NSF MRSEC are gratefully acknowledged.

PS-ThP13 Measurement of Electron Energy Probability Function in Dual-Frequency Capacitive Discharges, ***S.K. Ahn***, *H.Y. Chang*, Korea Advanced Institute of Science and Technology

Changes in plasma characteristics depending on low-frequency power in dual-frequency capacitive discharges were found from the measurement of electrical characteristics and electron energy probability functions (EEPFs). It is shown that as the low-frequency (2 MHz) power increases for the fixed high-frequency (27.12 MHz) current, the ion bombardment energy and the ion flux onto the electrode increase simultaneously, and hence independent control of the ion energy and the ion flux is hardly achievable in dual-frequency capacitive discharges. It is also shown that the coupling between the low-frequency power and the ion flux originates from change in electron heating mechanisms when varying the low-frequency power. Depending on the discharge pressure, changes in the collisional electron heating in the bulk plasma and participation of the secondary electron emission in the ionization process are observed.

PS-ThP14 Time-resolved Fast Imaging of the Arcing in RF Discharge*,* ***Y.H. Kim****, H.S. Lee, H.Y. Chang*, KAIST, Korea

Arcing have become a fatal problem in TFT-LCD fabrication, semiconductor manufacturing, PECVD, and many other processes using plasma. Although modern plasma processing is using rf power, the arcing in rf plasma isn't well-known. We investigated the arcing in RF plasma. In order to generate the arcing, the dc-grounded rf (13.56 Mhz) power was delivered to argon plasma. The arcs are generated at high plasma potential (over 100 V), irregularly. We measured floating potential, discharge current and voltage during the arcing, and sparks were observed in arcing spots. Floating potential drastically decreased to almost ground potential, and both discharge current and voltage decreased to almost zero, too. As soon as floating potential decreased to ground, floating potential, discharge current and voltage return to steady state slowly more than decrease. These arcing signals show that the arcing perturb the rf plasma and that rf plasma transiently response. The discharge of sheath-capacitor by collective electron emission explain the transient behavior of plasma during the arcing. And, to confirm the collective electron emission, we imaged the arcing by using the ICCD (intensifed charge coupled device, ANDOR Technology Ltd.) camera with the maximum gate speed of 2ns. We checked the three regions in the aring. These are sheath breakdown region, arcing duration region and shaeth rebuilding region.

PS-ThP15 Design of a Kalman Filter for Plasma Process State Estimation and Control*, B.J. Keville,* ***M.M. Turner***, Dublin City University, Ireland

Real time, closed loop control of certain plasma species may potentially improve reproducibility and increase process yields. In order to investigate the feasibility of applying closed loop control to a plasma process, closed loop control of a plasma simulation was studied. This presentation concentrates solely on control issues, since the simulation was described in a companion presentation. The design of real time control algorithms is facilitated by simple, dynamical process models. The derivation of such a model from a much more complex simulation is presented, together with a stability analysis which indicates how the parameters of a real time control algorithm may be determined from such a model (model-based control). Process measurements may be indirect and, in addition, corrupted by process and measurement noise. Simple dynamical models may be used to construct model-based estimators such as the Kalman filter. The construction of such a filter to improve estimates obtained from optical emission spectroscopy is described in this presentation. Finally, the application of adaptive control to maintain closed loop stability despite changes in process parameters such as wall sticking coefficient due to chamber seasoning is presented.

PS-ThP16 Contamination Detection through OES in Conductor Dry Etch Process*,* ***C. Bevilacqua****, A. Marchelli, P. Petruzza, G. Fazio*, Numonyx

In a R&D fab, where different processes are performed on the same dry etching hardware, there is a strong need to monitor the status of the chamber, in terms of cross-contamination from the different etching species and their reactions products deposited on chamber walls, which can cause uncontrolled shifts in the processes.

Through this work we validate a new technology method for monitoring and reveal metal elements in dry etch conductor tool.

Changes in chamber wall conditions (e.g., chemical surface composition) are identified as one of the main causes of process drifts leading to changes in the process performance (etch rates, etch profiles, selectivity, uniformity, etc.). This effect is particularly critic when the same chamber is required to sequentially process metals and non-metal elements. Standard control procedures mainly based on XRF technology utilize wafer tests to perform the acquisition measurements with relevant down times and low frequency testing. It is known that different conditions of the chamber walls have great influence upon global system impedance (plasma + equipment hardware), which requires continuous tuning of the RF system in order to maximize the power transfer to the plasma.

The observation of optical emission (performed through a spectrometer directly installed on the tool) from a waferless He plasma allows to detect some variation of impedance due to different chamber conditions.

The choice of He as process gas for this test is mainly due to the fact that it is chemically inert; besides is allows minimum impact on consumable parts inside the equipment. By comparing the test described to standard quantitative technology, we are able to identify a cut off threshold - technology device-dependent - above which the decontamination procedure becomes mandatory.

The new test can be used at the end of each critical process like a waferless autoclean, in order to constantly monitor the status of the chamber and assure a safe and correct lot processing.

PS-ThP17 Spatial Evolution of the Electron Energy Distribution Function in a Microwave Surface-Wave Plasma*,* ***J.P. Zhao****, R.V. Bravenec, L. Chen, M. Funk, R. Sundararajan,* Tokyo Electron America, Inc.*, C.Z. Tian, K. Ishibashi, T. Nozawa*, Tokyo Electron Technology Development Institute, Japan

Microwave surface-wave discharges operating within a wide power and pressure window can be used to produce large-area plasmas of densities exceeding 10^{11}/cm^3. Due to its inherent diffusion characteristics, away from the discharge source one can expect a relatively high density, quiescent, uniform, and low-temperature single Maxwellian plasma near the wafer region. That is, one would have a unique plasma tool with totally decoupled source of discharge and wafer process region. These merits are highly desired in large-area microelectronic technologies, such as in plasma-enhanced chemical-vapor deposition and etching processes. Because of these promising features, we are trying to understand the mechanisms of the microwave surface-wave plasma such as electron heating and power absorption in the discharge region and the spatial evolution of plasma parameters in the entire plasma volume. Understanding the evolution of plasma parameters in the entire plasma volume would help the development of tools based on microwave surface-wave plasmas and the design of process recipes. The plasma source used in this work consists of a radial line slot antenna (RLSA) which transmits 2.45 GHz microwaves into a large quartz resonator disk which then couples to the plasma. The plasma parameters of a nitrogen plasma, e.g., electron energy distribution functions (EEDF's) are measured using a cylindrical Langmuir probe. EEDF measurements are carried out from 8 mm below the bottom surface of the resonator disk to the wafer surface, a span of ~140 mm in the vertical direction. A wide pressure-power range has been investigated, i.e., pressures from 20 to 800 mT and powers from 2 to 4 kW. Based on initial global-modal analysis of experimental observations, EEDF's are analyzed using a curve fitting method developed in-house that assumes electrons in the microwave surface-wave plasma consist of two Maxwellian distributions and a drifting Maxwellian that models a beam component.[1] The relative population and magnitude of these electron components vary as a function of vertical location in the plasma volume. High populations of energetic electrons with energies exceeding 20 eV are typically observed near the resonator disk, i.e., the EEDF is dominated by the beam component. Away from the resonator disk, the EEDF transitions to two Maxwellians then thermalizes to a single cold Maxwellian of Te ~1 eV near the wafer surface. Pressure and power are found to have strong effects on the transition of the beam component to Maxwellian component. Particle-in-cell simulations[1] are conducted to understand the experimental observations.

[1] R. V. Bravenec et al., presentation at this conference.

PS-ThP18 Diagnostic Study of an rf-capacitively Coupled Plasma: The Breakdown of the Periphery Gap Regime*,* ***H.W. Chang****, C.C. Hsu*, National Taiwan University, Taiwan

A diagnostic study of a radio-frequency capacitively coupled plasma of Ar, O_2, N_2, and He was performed to investigate the mechanism that dominates the breakdown of the periphery gap region. This plasma chamber has a cylindrical glass chamber with annular ring-shaped, powered electrodes with an adjustable height and a planar sample stage that serves as the grounding electrode. A voltage probe and a current probe were used to monitor the electrical characteristics of this plasma, and an optical emission spectrometer was used to monitor the optical emission spectra of the plasma. It is shown that as the (peak-to-peak) voltage at the powered electrode exceeds a critical value, the ignition in the region between the glass chamber wall and the grounding electrode occurs. Such a breakdown potentially leads to unstable and non-uniform discharge. A drop of the current and voltage were found to accompany the periphery region breakdown, and it was found that the pressure, gas type, and gap size are the decisive factors that dominate such a breakdown. The breakdown voltage increases with the decreases of the gap and with the decreases of pressure: in an Ar discharge under 80 mtorr, the breakdown voltage increases from 280 to 972 V as the sample stage-glass chamber wall gap decreases from 7 to 5 mm. Under 5 mm gap and 100 mtorr, the voltage at which the periphery region breakdown occurs for Ar, N_2, and O_2 are 577, 1470, and 2444 V while no breakdown occurs in He plasmas with the voltage up to 2560 V. While such a breakdown seems undesired in materials processing, we will show that a well-controlled transition could potentially be used to obtain a localized high-density region that could be useful for materials processing.

PS-ThP19 Real-Time Feedback Control of Radical Species by OES in a VHF Plasma for Microcrystalline Silicon Thin Film Deposition, ***C.H. Chang****, C.C. Du, M.W. Liang, J.R. Huang,* Industrial Technology Research Institute, Taiwan*, Y.L. Chang, K.C. Leou*, National Tsing Hua University, Taiwan

Plasma deposition of intrinsic microcrystalline silicon (μc-Si:H) films with high deposition rates is a key process for the fabrication of high efficient thin-film solar cells. Recent studies have shown that the concentration of the radical species in hydrogen diluted silane plasma is time-dependent during the deposition process and results in inhomogeneous film growth that diminishes the solar cell efficiency. In this study, we developed a real-time feedback control system that corrects for the radical species variation in a VHF (40.68 MHz) PECVD reactor, via modulating the chamber pressure and silane dilution for depositing high quality μc-Si:H films. In this control system, trace rare gases-optical emission spectroscopy (TRG-OES) was used to determine the absolute species concentrations (e.q. Si, SiH_x, H) by deriving from their optical emissions. To convert the emission intensities into absolute number densities, a small amount of Ar was fed into the plasma to be as trace gas. Observed real-time variations in species signals were then compensated by using a proportional-integral (PI) feedback control algorithm. The system actuator was either or both of the pressure controller and the silane mass flow controller. The experimental results show that the OES intensities have obvious spikes after plasma is ignited and then decreases to a lower level at the first stage in about 10 seconds. This is because of the pressure unbalance between the throttle valve control and the expanded number density of gas induced by plasma heating and dissociation reaction in the chamber. After the transient of pressure unbalance, the intensity of H_α increases close to 20 % and the SiH^* decreases 10 % during the deposition in 10 minutes. This is believed to be due to the change of chamber wall surface condition. The deposited silicon films on the rf electrode, glass substrate and the other surface surrounds the plasma, grow continuously and affect the conditions for plasma. In the mean while, the closed-loop control can indeed stabilizes the radical species concentration within ± 1.5 % and has a good crystallinity control during the deposition process. Comparisons such as film growth structure and efficiency of solar cells deposited by closed-loop and open-loop controls will also be presented at the conference.

Surface Science
Room: Hall 3 - Session SS-ThP

Surface Science Poster Session

SS-ThP1 Ordered 2-D Structure of Si(337)-4×1 Induced by C Incorporation into Si(5 5 12)-2×1, ***H. Kim****, O. Dugerjav, G. Duvjir, H. Li, J.M. Seo*, Chonbuk National University, Republic of Korea

Using STM, it has been found that Si(5 5 12)-2×1 composed of tetramer (T) / dimer-adatom (D-A) rows and π-bonded (π) / honeycomb (H) chains [Surf. Sci. **601**, 1831 (2007] is transformed irreversibly to an ordered (337)-4×1 terrace with (113) facets through adsorbing C_2H_2 at 650℃ followed by post-annealing at 750℃. The transformation from (5 5 12) to (337) starts from a T row and a π chain in the (5 5 12) surface, and simultaneously the rest part of (5 5 12) converts to T rows and π chains, which will be transformed to (337). By Si 2*p* and C 1*s* core-level photoemission studies using synchrotron radiation, it has been confirmed that such an irreversible structural transformation is due to subsurface C atoms. If the (337) terrace is only composed of T rows and π chains with a 2× periodicity, the compressive stress exists so that the (337) terrace becomes unstable. However, subsurface C atoms release this compressive stress through breaking 1-D structures and change to a stable surface composed of 4×1 dot structures. The detailed atomic structures of the 4×1 surface and the steps of transformation will be presented.

SS-ThP2 Surface Passivation by Sb Adsorption: Sb/Si(114)-2 × 2, *O. Dugerjav, H. Kim, G. Duvjir, H. Li,* ***J.M. Seo***, Chonbuk National University, Republic of Korea

Sb adsorption on the Si(114)-2×1 surface [composed of dimer (D), rebonded-atom (R), tetramer (T) rows] at 600 ℃ has been investigated by STM and synchrotron photoemission spectroscopy (PES). When the Sb coverage exceeds 0.25 ML, two periods of 2×1 [(D-R-T)-(D-R-T)] is transformed to 2×2 [D-R-D-R-R_{Sb}-D-$R_{Sb,}$ where R_{Sb} means an R row replaced by deposited Sb atoms]. Such a transformation turns out to be nanofaceting to 2×(115) and 2×(113) and is originating from the stress balance between the tensile rebonded D_B-type D(6)-R(5)-D(6)-R(5) rings [Phys. Rev. Lett. 77, 687 (1996)] and the compressive R_{Sb}(5)-D(7)-R_{Sb}(5) rings [Sur. Sci. **411**, 54 (1998)]. This Sb-adsorbed 2×2 surface has 37.5% less dangling bonds and 0.27 eV less band-bending than the clean surface. It has been found that the addimer adsorbs exclusively on the D(7)-R_{Sb}(5) ring site, which implies that the critical condition for addimer adsorption is the relative angle between dangling bonds of D(7)-R_{Sb}(5) rings.

SS-ThP3 *In situ* Attenuated Total Reflectance and Transmission Fourier Transform Infrared Spectroscopy of (tetrakis)dimethylamido Hafnium (IV) Decomposition and Adsorption Dynamics on H-Si(100) Surface, ***K. Li****, N. Li, T.M. Klein*, The University of Alabama

Low temperature atomic layer deposition (ALD) is favored for more uniform thin film. The authors have investigated the surface reaction mechanism of first step of Hf ALD agent tetrakis(dimethylamido)hafnium (TDMAH) reacting on the H-Si(100) surface for low temperature range 60-250ºC by *in situ* ATR-FTIR. The formation H-Hf species was observed in the chemisorbed layer and a gas phase initiated adsorption mechanism was hypothesized by *ab initio* calculation. *In situ* transmission FTIR will be used to monitor the gas phase decomposition dynamics and products of TDMAH. Two most possible reactions: insertion and β-hydride elimination are expected to be observed. Deuterium water prepared background will be used to verify the Hf-H species on H-Si(100). Interfacial bonds of Hf-N and Hf-Si are to be of about 1:1.5 in concentration from thermodynamic calculation. Minor C-Si bond from silylation by product is expected to be observed during desorption. Experimental measurement of decomposition rate will be compared with the *ab initio* kinetic data.

SS-ThP4 Exploring Photomechanically Switching Molecules on Semiconductor Surfaces, ***J. Cho****, L. Berbil-Bautista, N. Levy, D. Poulsen, J.M.J. Fréchet, M.F. Crommie*, UC Berkeley

The photomechanical switching behavior of organic molecules changes dramatically when the molecules are placed on a surface. Metal surfaces, for example, often quench or slow photomechanical activity due to strong molecular interaction with continuum electronic degrees of freedom. Semiconductor surfaces are expected to induce very different molecular switching behavior due to the presence of a band gap, potentially resulting in longer excited-state lifetimes and enhanced control of photomechanical properties. We have explored the local structure and self-assembly of photomechanical molecules on the semiconducting GaAs(110) surface using variable temperature scanning tunneling microscopy. We will report on the nanoscale response of azobenzene derivatives on GaAs to optical irradiation in the UV-vis spectral regime.

SS-ThP5 Photo-induced Reactions of Alanine Adsorbed on Permalloy: A Real Time X-ray Photoelectron Spectroscopy Study, ***V. Kalyanaraman****, R.A. Rosenberg*, Argonne National Laboratory*, P.J. Ryan*, Ames Laboratory*, M. Abu Haija*, Argonne National Laboratory

Recently it was demonstrated that chiral selective chemistry can be induced by spin-polarized electrons from a magnetic substrate. The C-O bond cleavage rate in adsorbed 2-butanol showed a 10% enhancement depending on the chirality of the molecule and spin polarization of the substrate secondary electrons(1). We have recently extended this research to alanine (CH_3CHNH_2COOH), the simplest chiral amino acid. Our initial work examined the x-ray induced photolysis of alanine adsorbed on a thick Permalloy film by monitoring changes in the C1s and N1s photoelectron spectra as a function of irradiation time. Alanine was shown to adsorb in both zwitterionic (~2/3) and neutral (~1/3) forms on Pd(111)(2). C1s and N1s x-ray photoelectron (XP) spectra of alanine adsorbed on Permalloy at 200 K indicate similar adsorption behavior. Irradiation of the adsorbate with x-ray photons results in changes in both the C1s and N1s XPS data, which we attribute to C-C bond fission at the chiral carbon desorbing CO_2 and/or CO from the COO- moiety, and leaving behind ethylamine and/or HCN. Strong support for this assignment comes from similar intensity variations in the C 1s and N 1s XP spectra from D-alanine on Pd(111) as the substrate temperature was increased above room temperature(2). Future work will be devoted to determining if the observed x-ray induced reaction rates are sensitive to the alanine chirality and the polarization of the secondary electrons from the underlying substrate.

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.

References

(1) R. A. Rosenberg et al., Phys. Rev. Lett. **101** (2008) 178301.

(2) Feng Gao et al., Surf. Sci. **601** (2007) 3276.

SS-ThP6 Trajectories and Neutral Fractions of Alkali Ions Scattered from Au(788), ***R.E. Lake****, M.P. Ray, C.E. Sosolik*, Clemson University

Stepped metal surfaces are natural systems for studying lateral quantum confinement [1]. Au(788) is a surface vicinal to the (111) plane that reconstructs and forms stable 3.8 nm wide periodic monatomic steps with (111) orientation. Step edges terminate in {111} microfacets. Electron wave functions are confined laterally in a direction perpendicular to the steps and contribute a 1D-like quantum well state to the Au(111) electronic structure. To probe this structure-property relationship we scatter hyperthermal energy alkali ions from the surface and measure the energy and neutral fraction of the scattered ions. By analyzing our data with the classical trajectory simulation SAFARI, ions scattered from the steps can be clearly distinguished from the step edge scattering events. The neutral fraction of scattered alkali ions is sensitive to the electrostatic potential directly above a scattering site and can detect quantum confined states [2]. Measured neutral fractions for different species of alkali ions are interpreted with a model of multi-state resonant charge transfer.

[1] A. Mugarza, A. Mascaraque, V. Perez-Dieste, V. Repain, S. Rousset, F. J. Garcia de Abajo and J. E. Ortega. Phys. Rev. Lett. **87**, 107601 (2001).

[2] G. F. Liu, Z. Sroubek and J. A. Yarmoff. Phys. Rev. Lett. **92**, 216801 (2004).

SS-ThP7 Probing Diffusivity in Nanoscale Supercooled Liquid Films using Rare-Gas Atoms, ***J. Matthiesen***, *R.S. Smith, B. Kay*, Pacific Northwest National Laboratory

Molecular beams, temperature programmed desorption, and infrared spectroscopy were used to study the diffusivity in nanoscale supercooled liquid films of alkanes and alcohols. Amorphous films were grown on top of a layer of rare-gas atoms on a Pt(111) substrate at 25 K in UHV. As the films are heated they transform from amorphous to supercooled liquid films around the glass transition temperature. The rare-gas atoms were found to diffuse through the films in the supercooled liquid state. In a series of experiments, the layer thickness and heating rate were varied to extract diffusivities over a range of different temperatures. Numerical simulations of the rare-gas atoms diffusing through the supercooled films were used to quantitatively model the experimental results. Mixing of initially layered isotopically labeled alcohol and alkane films were also performed. The extracted diffusivities for the rare-gas atoms were in good agreement with the self-diffusion coefficients extracted from the experiments with isotopically labeled species. 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.

SS-ThP8 Adsorption of Metal Phthalocyanines on Cu(111) and Cu(100): A STM Study, ***S. Chang***, *J. Brede, J. Schwöbel, S. Kuck, G. Hoffmann, R. Wiesendanger*, University of Hamburg, Germany

The temperature dependent adsorption behavior of 4-fold symmetric metal phthalocyanines (MPcs) on metals with commensurate and incommensurate symmetries was investigated by means of scanning tunneling microscopy. On the 4-fold symmetric Cu(100) surface, planar and 4-fold molecular structures in two equivalent orientations were found for MPcs when prepared at room temperature. In addition, two metastable orientations were identified when prepared at low temperature which can be depopulated upon annealing. MPcs adsorbed on the 6-fold symmetric Cu(111) surface showed a disturbed molecular appearance. The symmetry of molecular structures changed from 4-fold to 2-fold which is discussed in terms of molecule-substrate interaction.

This work was supported by the DFG within the GrK 611 and the SFB 668-A5 and by the European Union in the project “SPiDMe”.

SS-ThP9 Iron Phthalocyanine on the Ag(111) Surface: Structure and Electronic States, ***K.W. Hipps***, *T. Takami, C.E. Carrizales*, Washington State University

Epitaxial growth of iron phthalocyanine on a silver (111) surface has been studied with scanning tunneling microscopy in ultrahigh vacuum. Commensurate two-dimensional ordering with parallelogram unit vectors (**b**1, **b**2) where **b**1 = 5**a**1 + 2**a**2 and **b**2 = 5**a**2, where **a**1 and **a**2 are unit vectors of Ag(111) surface, were observed. The parallelogram structure was more commensurate than those of FePc on Au(111) or graphite and of CuPc on Ag(111), and the surface density is greatest on Ag(111). The orbital mediated tunneling spectra showed a first ionization potential at 5.1 eV, similar to that in cobalt phthalocyanine on Au(111) surface.

SS-ThP10 Adsorption, Self Assembly, and Electronic States of Corrole Molecules Adsorbed on Different Copper Facets, ***L. Lichtenstein***, *S. Kuck, G. Hoffmann, R. Wiesendanger*, University of Hamburg, Germany

A new member of the metalloporphyrinoid class is the one-carbon short corrole which is a very accessible, easily tunable compound with many potential applications in material science and catalysis. These molecules differ from the parent porphyrin molecules [1] mainly by their lower inherent symmetry and the smaller cavity. In this study using STM we address the conformation (orientation and chirality) and self assembly of iron-triphenylcorrole (FeTPC) molecules on Cu(100) and Cu(111). At low coverage FeTPC molecules show restricted symmetry and can be controllably switched among different conformations [2]. At higher coverage formation of regular aggregates can be observed. We will present the results of the growth study in dependence of surface geometry and coverage and discuss results of scanning tunneling spectroscopy investigations of these systems.

[1] W. Auwärter et al., "Molecular nanoscience and engineering on surfaces", Int J. Nanotechnology Vol. 5, 1171 (2008).

[2] S. Kuck et al., "Naked" Iron-5,10,15-triphenylcorrole on Cu(111): Observation of Chirality on a Surface and Manipulation of Multiple Conformational States by STM, J. Am. Chem. Soc., 130, 14072 (2008).

This work was supported by the DFG within the GrK 611 and the SFB 668-A5 and by the European Union in the project “SPiDMe”.

SS-ThP11 One and Two Dimensional Structures of Water on Cu(110) and O/Cu(110)-(2x1) Surface, *B.Y. Choi,* ***Y. Shi***, *M. Salmeron*, Lawrence Berkeley National Laboratory

The interaction of water molecules with single crystalline surfaces provides a model for a fundamental understanding of the wetting properties of metals. We investigate one and two dimensional water structures on a clean and on an oxygen precovered Cu(110) surface using scanning tunneling microscopy and non-contact atomic force microscopy. In previous work it has been proposed that at sub-monolayer coverage water forms pentagon based chain-like structure on the clean Cu(110) surface at low temperature. Water pentagons have a strong water-metal interaction as well as a minimal strain in hydrogen bond[1]. On an oxygen precovered Cu(110) surface, hexagonal based honeycomb structures are preferred to form along the Cu-O stripes. However, it is not clear whether the hexamers are composed of intact or half-dissociated water molecules[2]. We will discuss how the Cu-O stripes affect the formation of the honeycomb structures and chains of water pentamers.

[1] J. Carrasco et.al Nature Mater. 8, 427 (2009)

[2] J. Ren et.al Phys. Rev. B 77, 054110 (2008)

SS-ThP12 Evaporation and Sliding of Water Droplets on Hydrophobic Coatings with Nanoscale Roughness, ***T. Furuta***, *A. Nakajima,* Tokyo Institute of Technology, Japan, *M. Sakai,* KAST, Japan, *T. Isobe,* Tokyo Institute of Technology, Japan, *Y. Kameshima,* Okayama University, Japan, *K. Okada*, Tokyo Institute of Technology, Japan

Hydrophobic coatings have been used widely to apply for various engineering products. For assessing these properties, static wettability such as the contact angle or sliding angle is not always a useful criterion for materials design. Recently, the recognition of the importance of dynamic wettability such as droplet’s sliding velocity or acceleration on a tilted surface has been growing gradually.

Water droplets are known to slide down on the hydrophobic solid surface by a caterpillar-like rolling motion with or without slippage at the solid-liquid boundary; a direct observation method for internal fluidity of sliding water droplets was established recently using particle image velocimetry (PIV). The contribution ratio of rolling and slipping motions to overall sliding acceleration reportedly depends on nanoscale roughness and chemical heterogeneity of the hydrophobic coatings.

On the other hand, evaporation is a fundamental phenomenon for liquids. Various studies have been conducted in relation to this phenomenon for liquid droplets on solid surfaces. Ultra-small, e.g. nanoliter-scale, droplets are evapolated and disappeared in a short time, which corresponds to a situation of large volume change ratio per unit period. It might possess similar dependence against nanoscale surface heterogeneity as well as dynamic wettability.

We prepared fluoroalkylsilane coatings with different nanoscale roughness. This study examined evaporation (including nanoliter-scale droplets) and sliding behaviors of water droplets on these coatings using an automatic microscopic contact angle meter and PIV method.

Evaporation and sliding behaviors of water droplets were investigated on smooth and rough coatings. Evaporation behaviors for these two coatings differed when nanoliter-scale droplets were used, although they were nearly identical for microliter-scale droplets. The droplets on the smooth coating exhibit greater sliding acceleration and a larger slipping velocity ratio than those on the rough coating. Both the evaporation behavior of nanoliter-scale droplets and sliding velocity of microliter-scale droplets were affected by nanoscale surface heterogeneity.

Moreover, considering power balance around the three phase contact area, line tension was measured for microliter-scale and sub-nanoliter-scale droplets of an ionic liquid on a highly smooth and homogeneous fluoroalkylsilane coating. Values for microliter-scale droplets were two orders larger than those for sub-nanoliter-scale droplets despite their identical combinations of solid surfaces and liquid. Scale factors related to this measurement and from the liquid play an important role in the discrepancy.

SS-ThP13 Passivation of Al(111) with Organic and Inorganic Adlayers

T. Yamada, RIKEN, Japan, *M. Kawai*, The University of Tokyo, Japan

Passivation of clean Al(111) has been attempted against oxidation in O_2 or air at room temperature by various kinds of adlayers prepared on the surface. The goal of this attempt is to block the growth of oxide layer by introducing a covering monolayer or thin multilayer, whose thickness is smaller than 1 nm. Metallic aluminum surfaces stored in air are usually covered with more than a few nm of Al oxide layer, which prevent us from fabrication of nanostructures and nanoparticles of pure metallic Al. If an ultrathin passivation layer, composed of inorganic or organic materials in a controlled manner, can inhibit oxidation of Al substrate, it will help enhancing the accuracy and precision of nano-scale fabrication. This approach was successful in passivating Si wafer surfaces [1]. When a clean Al(111) surface was exposed to pure O_2 gas at room temperature, the surface was covered with an amorphous oxide layer observed by low energy electron diffraction (LEED) and X-ray photoelectron spectroscopy (XPS) [2]. The thickness of oxide layer was calculated from XPS signal intensities, with referring to spectra of a cleaned sapphire (γ-Al_2O_3) surface. The process of oxide accumulation was once saturated below ~10^{-1} Torr of O_2 pressure, at which the thickness of oxide layer was <0.5 nm. Formation of such oxide layers was blocked with various kinds of thin adlayers, such as fluoride thin layers, alkanethiol monolayers etc., similarly to the formerly reported C_{60} layer [3]. At O_2 pressures higher than 10^{-1} Torr, another sort of rigorous oxidation process took place. The thickness of oxide layer was approximately proportional to the logarithm of O_2 exposure, reaching a few nanometers. Most of the monolayers from small precursor compounds could not block this process of oxidation. This process seems to involve penetration of O atoms deeply into the Al substrate. Practically, it is desirable to inhibit this rigorous process of oxidation. In this talk, we will present our attempts using monolayers including long linear molecules anchored on Al(111). The oxidation process was examined in the air up to the atmospheric pressure, involving O_2 and H_2O. Some kinds of adlayers on Al(111) were vulnerable in contact with H_2O. It is probably important to involve hydrophobic compounds to build a firm, oxidation-resistant monolayer.

[1] T. Yamada et al., *J. Electroanal.Chem.* **532** (2002) 247, T. Yamada et al., *J. Chem. Phys.* **121** (2004) 10660.

[2] H. Brune et al., *J. Chem. Phys.* **99** (1993) 2128, V. Zhukov et al., *Surf. Sci.* **441** (1999) 251.

[3] A. V. Hamza et al., *Surf. Sci.* **318** (1994) 368.

SS-ThP14 Reduction of Friction Drag by Superhydrophobic / Superhydrophilic Coatings

M. Sakai, Kanagawa Academy of Science and Technology, Japan, *A. Nakajima*, Tokyo Institute of Technology, Japan

Recently, the importance of controlling wettability on the solid surface is recognized in various industries. In the current paper, we evaluated friction drag of water on various surfaces including superhydrophobic / superhydrophilic coatings. The amount of friction drag was evaluated by the decrease of hydrostatic pressure during flowing in the tubes coated by various materials. When Reynolds number is smallest, superhydrophobic coating provides small friction drag. On the other hand, a superhydrophobic coating provided smallest friction drag when Reynolds number is 6000. The mechanism of this difference was discussed from the viewpoints of fluid mechanics and surface materials science.

SS-ThP15 Dynamic Solid-liquid Interaction on Hydrophobic Surfaces

N. Yoshida, The University of Tokyo, Japan, *M. Sakai*, Kanagawa Academy of Science and Technology, Japan, *A. Nakajima,* Tokyo Institute of Technology, Japan, *T. Watanabe*, The University of Tokyo, Japan

Dynamic solid-liquid interaction as a liquid droplet-movement on inclined hydrophobic~superhydrophobic surfaces was investigated. The liquid droplet movement was affected by a surface energy, roughness, and homogeneity of the solid surface, and furthermore it is revealed that the internal fluidity detected by Particle Image Velocimetry method changed the movement. On hydrophobic surfaces, the movement simply depended on contact angle if the solid surface had chemically and physically homogeneity. Surface inhomogeneity caused increases of contact angle hysteresis and internal fluidity, and then the droplet movement was observed to be decreased. In this presentation, we will discuss about the detail of relations among them.

SS-ThP16 Surface Reaction of Ozone with Alkali Halide Salts

T. McIntire, *J. Taing,* University of California, Irvine, *P. Ashby,* Lawrence Berkeley National Laboratory, *R.L. Grimm, A. Margarella, M.H. Cheng,* University of California, Irvine, *Z. Liu,* Lawrence Berkeley National Laboratory, *J.C. Hemminger*, University of California, Irvine

Heterogeneous reactions involving the oxidation of the halide components of sea-salt aerosols with trace atmospheric gases (*e.g.*, ozone, hydroxyl, and NO_x) have been proposed to be responsible for the release of active halogen species into the gas phase. While such halogen containing species have been observed in the marine boundary layer by field studies, the detailed mechanisms of the heterogeneous reactions leading to halogen release from sea salt aerosols are not well understood. In this work, reactions of gas phase ozone with alkali halide single crystals were studied at varying ozone and water vapor concentrations. Changes in the alkali halide salts were measured using transmission FTIR, x-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). While previous investigations found single crystals of KI oxidize to form a passivating layer of KIO_3 crystallites, the present study notes the loss of reactants with no observed surface-phase oxidized species, AFM experiments show that ozonolysis of KBr single crystals leads to roughening of step edges and the formation of etch pits which appears to depend on the amount of water vapor present. XPS spectra show a decrease in interfacial bromide believed to be concomitant with the etching observed in the AFM studies. Implications for the role of water on the reaction of gases such as ozone with alkali halide single crystals are discussed.

SS-ThP17 Evolution of Microscopic Surface Deformation on Si(111) due to Low Energy Ion Bombardment

P. Piercy, *J.M. David, D. Pohl*, University of Ottawa, Canada

Low energy ion bombardment of a crystalline solid may cause a variety of surface and subsurface damage. At moderately elevated sample temperatures to prevent amorphization, the sputtering process may leave a step-and-terrace morphology, but surface reconstruction may be disordered and a distribution of ion-induced defects may remain in a shallow, inhomogeneously strained, subsurface layer. After low energy argon ion bombardment on Si(111), we use a spot profile analysis of low energy electron diffraction data at in-phase conditions to measure a low amplitude, continuous distribution of surface height, which occurs in addition to atomic-height steps and other short-range atomic disorder at the surface. Measurements over a range of ion dose, ion energy, and sample temperature, are attributed to surface deformation due to strain around subsurface defects. For bombardment of the Si(111) surface at 600K by 230 eV argon ions with dose increasing in the range 10^{15}-10^{16} cm^{-2}, we find a continuous surface height distribution, whose contribution to the interface width increases from hundredths of an Angstrom up to ≈ 0.1 Å, correlated laterally over tens of Angstroms. These results may be interpreted in terms of an elastic continuum model of the solid, with defects created below the surface by independent ion bombardment events modeled simply by a distribution of small inclusions. At a higher surface temperature of 800 K, the surface deformation after the same ion energy and doses as above gives interface width contribution w increasing to 0.07 Å; with further bombardment to a dose of 10^{17} cm^{-2}, w grows to 0.15 Å. At a higher ion beam energy of 730 eV, w increases to a saturation value of 0.18 Å after an argon ion dose of $\approx 2 \cdot 10^{16}$ cm^{-2}. Implications for the evolution of the buried defect distribution will be discussed.

SS-ThP18 Ordering Mechanisms of Stripe Arrays on B-doped Si(100)

I. Ermanoski, *N.C. Bartelt, G. Kellogg*, Sandia National Laboratories

We have used low energy electron microscopy (LEEM) to study in real time the self-assembly of periodic stripe arrays on atomically flat Si(100) with high boron doping. Stripes consist of extremely elongated vacancy islands of single atomic height, formed at ~900ºC, confined in micrometer-sized pits. We have been able to create highly ordered arrays of straight, parallel stripes (in pits of up to ~8 μm in size) formed by allowing various defects to heal over relatively long periods of time. To allow this equilibration to occur, sublimation was compensated for by an external Si doser, allowing observation of stripe evolution over the course of hours, with no net loss or gain of Si from the area of interest. Equilibrium stripes are very uniform in width and periodicity, and exhibit the greatest stability at 0.5 monolayer coverage. Observed stripe formation and ordering mechanisms include spontaneous nucleation and growth of new stripes, longitudinal splitting, as well as coarsening due to surface diffusion. Stripe periodicity depends on temperature, allowing for control of this property. Stripes form in a temperature range of ~100C, outside of which they assume the familiar shape of elongated islands. Stripe order can be preserved to room temperature by quenching.

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.

SS-ThP20 Degradation of Semiconductor Photoelectrode Surfaces in Aqueous Environments from *ab-initio* Molecular Dynamics, ***B. Wood***, *T. Ogitsu, E. Schwegler*, Lawrence Livermore National Laboratory

Among currently known approaches for hydrogen production, catalytic splitting of water molecules using semiconductor-based photoelectrochemical (PEC) devices has garnered particular interest, with reasonably high efficiencies already demonstrated in laboratory conditions. Unfortunately, these materials often evidence extremely facile surface corrosion, severely limiting their practical use in real-world devices. Currently, a clear understanding of this corrosion process at the water-semiconductor interface and its damaging effect on catalytic activity is lacking. Although certain theoretical efforts have attempted to address this issue, these studies have generally focused on zero-temperature gas-phase molecular adsorption, forgoing a realistic model of the liquid-solid interface. Accordingly, we have performed extensive *ab-initio* molecular dynamics simulations to probe the structure, chemistry, and dynamics of the water-electrode interface for model semiconductor systems in a realistic aqueous environment. Our work has focused on InP and GaAs, which, although structurally and functionally similar, exhibit substantial differences in terms of stability in an aqueous environment and in surface reactivity. These calculations are able to provide a unique in-depth understanding of surface

structure and transport. As such, they promise to provide a crucial first step towards understanding the complexities of the atomistic processes involved in hydrogen evolution and PEC corrosion.

Thin Film
Room: Hall 3 - Session TF-ThP

Aspects of Thin Films Poster Session

TF-ThP1 Ultra Thin Cermet Resistor Films Deposited by DC Magnetron Sputtering, ***V.V. Felmetsger***, Tegal Corporation

Technological solutions for producing nanoscale cermet resistor films with sheet resistances above 1000 Ω /□ (Ohm per square) and low temperature coefficients of resistance (TCR) have been investigated. 2 to 40 nm thick films were sputter deposited from $CrSi_2$-Cr-SiC targets by a dual cathode dc S-Gun magnetron. In addition to studying film resistance versus temperature using four point probe measurements, scanning electron microscopy and atomic force microscopy were also employed for analysis of the nanofilm structure features. This study has revealed that the cermet film TCR displays a significant increase when the deposited film thickness is reduced below 2.5 nm. An optimized sputter process consisting of wafer degassing, cermet film deposition at elevated temperature with rf substrate bias, and a double annealing in vacuum consisting of an in situ annealing following the film sputtering and an additional annealing following the exposure of the wafers to air has been found to be very effective for the film thermal stabilization and for fine tuning the film TCR. Cermet films with thicknesses in the range of 2.5 - 4 nm deposited using this process had sheet resistance ranging from 1800 to 1200 Ω /□ and TCR from – 50 ppm/˚C to near zero, respectively. A possible mechanism responsible for the high efficiency of annealing the cermet films in vacuum (after preliminary exposure the films to air) resulting in resistance stabilization and TCR reduction is discussed.

TF-ThP2 Formation of DLC Films by Inert-gas Ion Beam Assist in a $C_{10}H_8$ Atmosphere, ***S. Narita***, *I. Takano*, Kogakuin University, Japan

Diamond-like carbon (DLC) has the amorphous structure that is chiefly composed by graphite (sp^2) and disordered graphite (sp^3) state. Therefore mechanical property of DLC generally shows high hardness and low friction. DLC film has been prepared by various method of chemical vapor deposition (CVD) or physical vapor deposition (PVD) including the sputtering method. Commercial application of DLC has been already performed as engine parts of an automobile or surface coating of a hard disk.

In this study, DLC films were formed using Ar^+ or He^+ ion beam assist in a naphthalene ($C_{10}H_8$) atmosphere. $C_{10}H_8$ is aromatic hydrocarbon with two benzene rings of a solidly in normal temperature and pressure. In our previous study, toluene (C_7H_8) of aromatic hydrocarbon with one benzene ring was used at same experimental process. By using $C_{10}H_8$ as an atmosphere gas, the higher deposition rate is expected than C_7H_8 gas. The formation conditions of DLC were changed with ion beam accelerating voltage and current density. Current dependence was performed by ion beam current density of 10 to 70 $\mu A/cm^2$ with a constant accelerating voltage of 5 kV, while voltage dependence was performed by 1 to 12 kV with a constant current of 10 $\mu A/cm^2$.

The mechanical properties of hardness and friction coefficient were determined using the dynamic micro Knoop hardness tester and the pin-on-disk tribo-tester with a SUJ2 ball of a 1/4 inches diameter, respectively. The conditions of examination were fixed at a load of 0.98 N, a revolution speed of 135 rpm, a sliding diameter of 10 mm and a sliding distance of 10 m. Atomic concentration and structure of the films were investigated by X-ray photoelectron spectroscopy (XPS) and Raman spectroscopy, respectively.

The suitable property of Knoop hardness and friction coefficient were obtained by conditions of accelerating voltage of 5 kV with current density of 10 $\mu A/cm^2$. Knoop hardness of the film showed 5.37 GPa using Ar^+ ion beam irradiation, while the friction coefficient of the film showed 0.117 using He^+ ion beam irradiation. It was clear that property of DLC film was changed by ion species. In the case of He^+ ion beam irradiation, low friction property was shown at 5 to 7 kV with 10 $\mu A/cm^2$, while high hardness property was obtained by Ar^+ ion beam irradiation of 5 kV with 10 to 40 $\mu A/cm^2$.

TF-ThP3 Amorphous Carbon-Gold (a-C:Au) Thin Films, ***Z. Montiel***, *S.E. Rodil, S. Muhl,* Instituto de Investigaciones en Materiales-Universidad Nacional Autonoma de Mexico, *L. Rodriguez*, Instituto de Fisica-Universidad Nacional Autonoma de Mexico

Amorphous carbon-Au (a-C:Au) composite thin films were synthesized by co-sputtering using a graphite target with an attached piece of pure gold. Under this configuration and depending on the deposition conditions and materials, it is possible to produce different structures; multilayers; nanocomposite thin films, or compounds. The aim of the work was to determine if by analysing the ellipsometric spectra of samples deposited on silicon substrates it would be possible to distinguish between the different structures. For this purpose, different deposition powers (40 to 130 W) were investigated, keeping the other deposition conditions. The film microstructure and composition were evaluated using X-ray diffraction (XRD) and Rutherford Backscattering (RBS).

As deposited films did not show any characteristic signal in the ellipsometric spectra related to the presence of gold, in agreement with the XRD results where no diffraction peaks were observed. Nevertheless, the RBS data showed that the gold concentration could be varied between 9 and 7 at% as the power increased. The samples were submitted to a thermal treatment in an Argon atmosphere at 600 °C, in order to promote the gold segregation. Ellipsometric spectra after the annealing clearly showed the absorption related to the interband transitions of gold (~ 2.5 eV). The spectra for each deposition power were modelled to obtain the variations in the optical properties of the films due to the gold incorporation, either as atomic inclusions (as-deposited samples) or particles (annealed samples) using Tauc-Lorentz models for the carbon matrix and the extended Drude-Lorentz dispersion model for the gold particles.

TF-ThP4 Influence of Non-uniformity and Surface Morphology of Sputtering Deposited CdTe Thin Films in a Large-area on Energy Conversion Efficiency of Solar Cells, ***J. Park***, *C. Lim, S. Ryu,* Chosun University, Korea*, N. Kim,* Chonnam National University, Korea*, W Lee*, Chosun University, Korea

The thin-film CdTe solar cell technology is theoritically well known that it can improve the conversion efficiency and production costs compared to the conventional silicon solar cell technology. Due to the optimal band gap energy (about 1.4eV) for solar energy absorption, high light absorption capability and low cost requirements for producing solar cells, CdTe has been widely researched as the suitable for the commercializ ation . In this study, the sputtering method, which can improve the cost-efficiency and mass production of solar cells, was employed to deposit the CdTe thin film on the large-area substrates with the various processing conditions such as gas pressure, power, and the distance to the target. The non-uniformity and surface morphology were analyzed using AFM and SEM in the large-areaed surface of CdTe thin-films deposited with the various processing conditions; likewise, the effects of the processing conditions on the non-uniformity and surface-morphology of the thin-film surface were compared. Also, the optical and electrical characteristics of CdTe thin films with the globally and locally difference in non-uniformity and surface morphology in a large-area were compared; thus, the effects of them on the efficiency of the sputter ing deposited thin film CdTe solar cells in a large-area were examined .

TF-ThP5 Spatial Resistivity Distribution of Transparent Conducting Impurity-doped ZnO Thin Films Deposited on Substrates by DC Magnetron Sputtering, ***J. Oda***, *J. Nomoto, M. Konagai, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

In this paper, we describe and discuss the relationship between two techniques developed for improving the spatial resistivity distribution of transparent conducting impurity-doped ZnO thin films deposited on glass substrates at 200^{o}C by dc magnetron sputtering (dc-MS) with various sintered impurity-doped ZnO targets. One improvement method superimposes an rf component onto dc-MS. The other improvement method uses conventional dc-MS with a low resistivity target prepared under optimized conditions. It was found that decreasing the resistivity of the targets used improved the resistivity distribution in both Al- and Ga-doped ZnO (AZO and GZO) thin films deposited using dc-MS either with or without superimposing rf power. The use of rf-superimposing dc-MS with lower resistivity targets did not result in a sufficient improvement in spatial resistivity distribution over that found in impurity-doped ZnO thin films deposited by conventional dc-MS with the same targets. With rf-superimposed dc-MS, the resistivity distribution in thin films only improved when using targets with a resistivity higher than around 1X10^{-3} Ωcm. In addition, the sintered targets optimized for preparing transparent conducting AZO and GZO thin films with lower resistivity as well as more uniform resistivity distribution on the substrate surface were found to exhibit a tendency for lower resistivity than around 1X10^{-3} Ωcm. Consequently, the observed improvement of resistivity distribution on the substrate surface when using the two deposition techniques was achieved by suppressing the amount and/or activity of oxygen reaching the substrate surface during the deposition, resulting from a deposition using either a lower dc sputter voltage or a lower resistivity impurity-doped ZnO target with a lower oxygen content.

TF-ThP6 *In-situ* Analyses on Negative Ions in the Sputtering Process to Deposit Al doped ZnO Films, ***N. Tsukamoto**, D. Watanabe,* Aoyama Gakuin University, Japan, *N. Ito,* Panasonic Electric Works Co., Ltd., Japan, *N. Oka, Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Magnetron sputtering processes using ceramic oxide targets have been used to deposit transparent conductive Al doped ZnO films because of its advantages for large area uniform coatings with high packing density and strong adhesion. However, the degradations of electrical properties and crystallinity for ZnO films have similarly been observed at the positions opposite to the erosion track on the target. These are considered to be caused by the bombardment of high energy particles such as energetic Ar atoms (high energy neutrals) or negative oxygen ions. In this study, we tried to detect the flux and energy distributions of high energy negative ions during the dc magnetron sputtering using an AZO target and discussed the influence of high energy negative ion bombardments on the structure and electrical properties of the films.

High energy negative ions were analyzed using a quadrupole mass spectrometer combined with an electrostatic energy analyzer, which was positioned at the substrate position opposite to the AZO (Al_2O_3: 2.0 wt%) target. The sputtering power during the analyses was maintained at 50 W. The O_2 flow ratio [O_2 / (Ar+O_2)] were controlled from 0 to 5 %. For the analysis of the flux of the negative ions at the different substrate locations, the sputtering target was perpendicularly moved to the quadrupole mass spectrometer. In order to control the cathode voltage, the magnetic field strength was selected as 0.025, 0.06 and 0.1 T. In order to discuss the influence of the bombardments on the film properties, AZO films were deposited on unheated alkali-free glass substrate under the same condition of the fragment analysis. The atomic oxygen negative ion (O^-) was observed as the high energy negative ions which possessed the energy corresponding to the cathode sheath voltage. The maximum flux of O^- was observed at the location opposite to the erosion track on the target. The flux of O^- decreased slightly with increasing O_2 ratio. These results indicate that high energy negative ions were not formed by electron attachment in the cathode sheath region but should be sputtered from the target surface. Depending on the magnetic field strength, the cathode voltage varied from 337 V at 0.1 T to 403 V at 0.025 T. While the peak of O^- shifted to lower energies with increasing the magnetic field strength, the flux of O^- was hardly changed. The lower the energy of the peak of O^- which AZO films is deposited at is, the lower both of resistivity and crystallinity for AZO films which are deposited at the positions opposite to the erosion track on the target are.

TF-ThP7 Properties of Si-DLC Thin Films Prepared by Ion Beam Assist in a $C_{12}H_{26}$ Atmosphere, ***T. Hara**, I. Takano*, Kogakuin University, Japan

DLC (Diamond-like Carbon) classified in new materials is amorphous carbon including hydrogen and has the similar property to diamond. DLC film was formed by the ion beam evaporation method in the early 1970's 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 shows the high hardness and low friction coefficient, DLC is applied in various fields such as motor parts or tools. Also the electric property of DLC is anticipated as material of a field emission source.

In this study, mechanical properties were investigated about Si- doped DLC thin films prepared by using ion beam and electron beam evaporation in a $C_{12}H_{26}$ atmosphere . The formation of DLC thin films was performed by assist of He$^+$ ion-beam irradiation in a $C_{12}H_{26}$ atmosphere and doping of Si into DLC was performed by electron beam evaporation. In this experiment, Si concentration in DLC was changed by control of an electron-beam evaporation source, while He$^+$ ion beam was irradiated at a constant accelerating voltage of 5 kV with a current density of 20 μA/cm^2. Film composition and microstructure 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 of 0.98 N until the sliding distance reached to a length of 100 m.

The improvement of mechanical properties for Si-doped DLC thin films was exhibited in this experiment. Knoop hardness of the DLC thin film with Si concentration of about 40 percent showed 8.2 GPa. Friction coefficient of the DLC thin film with Si concentration of about 24 percent showed 0.107 at sliding distance of 100 m. Each property corresponds to increase of about 46 percent in hardness and decrease of about 74 percent in friction coefficient as compared with un-doping DLC thin film prepared with an accelerating voltage of 5 kV at a current density of 20 μA/cm^2.

TF-ThP8 Influence of Microstructure and Surface Morphology on Photofunctional Properties of Titanium Dioxide Film Prepared by Reactive Magnetron Sputtering, ***K. Tanaka**, I. Takano*, Kogakuin University, Japan

Since the photoinduced decomposition of water on TiO_2 electrodes was discovered, semiconductor based on photocatalyst has attracted extensive interest. 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 as an energy source can provide an abundant photons, however, UV energy in the sunlight accounts for only a small fraction (～5%) compared to the visible region (45%). Many techniques have been examined to achieve the purpose, i.e. harness of the visible light. Improvement of TiO_2 has been performed by doping transition metals or anionic species, but these doped materials induce thermal instability and an increased number of carrier recombination centers. On the other hand, the relationship between structure and photofunctional properties of TiO_2 has some unclear points. Different TiO_2 structures can be obtained in the reactive magnetron sputtering method by control of O_2 gas flow rate and formation temperature.

In this study, TiO_2 was prepared by reactive magnetron sputtering using Ti target in an Ar/O_2 gas mixture. Composition and microstructure of these TiO_2 films were investigated by XPS and XRD, respectively. The surface morphology of TiO_2 was observed by AFM. Chromatic change of a methylene blue solution was applied as photofunctional property. Light irradiation to TiO_2 in a methylene blue solution was carried out using a commercial sterilizing lamp as UV light and an artificial sunlight lamp (with UV filter) as visible light. Transmittance of a methylene blue solution was measured by a spectrophotometer.

As results of XRD, the crystal structure of TiO_2 turned from a ruttile type into an anatase type by each increase of O_2 gas flow rate and formation temperature (100~300℃). In addition formation temperature had a large effect on TiO_2 surface morphology and roughness. The TiO_2 film prepared with high formation temperature showed a smooth surface. In the case of 300℃ in formation temperature, the higher photofunctional property under irradiation of UV light was obtained at an anatase type (O_2 gas flow rate of 2.5 sccm). In the case of visible light, lower photofunctional property was shown as compared with the case of UV light. However, photofunctional property showed the maximum value at a ruttile type (O_2 gas flow rate of 1.0 sccm) in visible light. The mutual relationship between the photofunctional property and the formation condition was dependent on not only the film structure but also the surface morphology.

TF-ThP9 High Rate Deposition of SnO_2-based Transparent Conductive Films by Reactive Sputtering with Impedance Control Method, ***Y. Muto**, Y. Nishi, K. Hirohata, N. Tsukamoto, N. Oka, Y. Sato,* Aoyama Gakuin University, Japan, *Y. Iwabuchi, H. Kotsubo,* Bridgestone Corporation, Japan, *Y. Shigesato*, Aoyama Gakuin University, Japan

SnO_2-based transparent conductive oxide (TCO) films have been used as transparent electrodes especially for solar batteries. Recently, because of the toxicity and shortage problems of In, SnO_2 is considered to be one of the ITO-alternatives. Most of the TCO films have been deposited by magnetron sputtering using oxide ceramic targets in industry, however, the deposition rate is not so high and also the cost for the high quality ceramic targets is high in general. On the other hand, reactive sputtering using metal or alloy targets should be one of the most promising techniques to achieve much higher deposition rate for various industrial applications because sputtering yield of the metallic surface is much larger than the one of the oxide surface and also the higher sputtering power density can be applied for metallic targets because of their higher thermal conductivity. The reactive sputtering process is strongly affected by the O_2 flow ratio; where the deposition rate exhibits hysteresis with respect to the O_2 reactive gas flow rate. Such behavior originates in the oxidation state of the target surface, resulting in the marked decrease in deposition rate with the increasing O_2 flow (transition region). Therefore, the sputtering conditions should be precisely controlled so as to obtain high-quality SnO_2-based TCO films by reactive sputtering with a high deposition rate and with high reproducibility.

In this study SnO_2 films doped with Sb or Ta (ATO or TTO, respectively) were deposited on unheated or heated glass substrates at 200^{o}C by the reactive sputtering with Sb-Sn or Ta-Sn alloy targets using a plasma control unit (PCU) and mid-frequency (mf, 50kHz) pulsing. PCU feedback system (Fraunhofer Institut fur Elektronenstrahl-und Plasmatechnik, FEP) monitors the oxidation states of target surface by observing in cathode voltage (impedance control method) [1]. The mf pulsing possesses the approximate shape of a square wave which make it possible to reduce arcing on the target when high power density is applied. In the case of the ATO films deposition on heated substrate at 200^{o}C in the "transition region", the deposition rate was 280 nm/min where the lowest resistivity of the ATO films was 4.6×10^{-3} Ωcm and the optical transmittance was more than 80% in the visible region.

[1] M. Kon, Y. Shigesato, et. al, Jpn. J. Appl. Phys. 41, 814 (2002).

TF-ThP10 Fabrication of Gallium Oxide Films using Ion-Beam Assisted Deposition, ***T. Ichinohe**,* Tokyo National College of Technology, Japan*, M. Ohshima, S. Masaki, T. Kawasaki,* TDY Inc., Japan*, M. Obinata,* TOHNIC Inc., Japan*, S. Takeda, H. Hino*, Nippon Light Metal Company, Ltd., Japan

Gallium oxide (β-Ga_2O_3) has been known to be one of transparent conductive oxides, being tin doped. In this study, gallium oxide films were fabricated by ion-beam assisted deposition. Oxygen ions accelerated at 70-200 eV were employed during deposition. According to X-ray diffraction (XRD) analyses, the as-grown films being amorphous, polycrystalline β-Ga_2O_3 was formed after heat-treatment over 500°C in nitrogen gas ambient. The films assisted in high energy ions tend to show sharp XRD peaks after heat-treatment. The films containing SnO_2 after heat-treatment at higher temperature (900°C) showed the same crystal structure although the peaks broaden. The ion-beam assisted films after heat-treatment showed high transparency from UV to near IR region.

TF-ThP11 Electrical and Optical Properties of Nb-doped TiO_2 Films Deposited by dc Magnetron Sputtering using a Slightly Reduced Nb-doped TiO_{2-x} Ceramic Targets*, Y. Sato, **Y. Sanno**, C. Tasaki, N. Oka,* Aoyama Gakuin University, Japan*, T. Kamiyama,* AGC Ceramics Co. Ltd., Japan*, Y. Shigesato*, Aoyama Gakuin University, Japan

Nb-doped anatase TiO_2 (Nb:TiO_2) films have attracted much attention as indium-free transparent conductive oxide films [1]. Recently, we have reported on electrical and optical properties of Nb:TiO_2 films deposited on glass substrate by dc magnetron sputtering using a slightly reduced TiO_{2-x} target with Nb_2O_5 pellets [2]. In this study, we investigated the effect of Nb doping on the electrical and optical properties of Nb:TiO_2 films with comparison of pristine TiO_2 films. Anatase TiO_2 and Nb:TiO_2 films were deposited on unheated quartz glass substrates by dc magnetron sputtering using a slightly reduced TiO_{2-x} ($x = 0.014$, conductivity: 3.7 Scm^{-1}) and Nb-doped TiO_{2-x} (Nb = 9.5 at.%) targets (AGC Ceramics, Japan). By using these reduced TiO_{2-x} targets, stable dc discharge was maintained because of the sufficient resistivity of the reduced TiO_{2-x} targets to avoid charge up of the target surface and hence to suppress arcing. X-ray diffraction patterns of all the as-deposited films exhibited amorphous structure, while they were crystallized into polycrystalline anatase structure after post-annealed in vacuum (6×10^{-4} Pa) at 500-600 ^{o}C for 1 hr. Electron probe microanalysis revealed that Nb concentration in the Nb:TiO_2 films remained almost constant at 7.4 at.%, regardless of O_2 flow ratio during the deposition. Resistivity of the TiO_2 films was larger than 1 Ωcm while the films were deposited at 5.0 % of H_2 flow ratio. In contrast, resistivity of Nb:TiO_2 films exhibited 6.3×10^{-4} Ωcm while the films were deposited at 0.10 % of O_2 flow ratio. Carrier density of the Nb:TiO_2 films was 2.0×10^{21} cm^{-3}, where the doping efficiency was estimated to be about 90%. All the annealed films possessed transmittance of over 60-80% in the visible region of light. Furthermore, transmittance of the Nb:TiO_2 films in the near infrared region decreased due to the shift of the plasma wavelength to smaller wavelength side with the increase in the carrier density caused by Nb doping. This work was partially supported by a High-Tech Research Center project for private universities with a matching fund subsidy from the Ministry of Education, Culture, Sports, Science, and Technology (MEXIT) of Japan.

[1] Y. Furubayashi et al., Appl. Phys. Lett. 86 (2005) 252101.

[2] Y. Sato, Y. Shigesato et al., Thin Solid Films 516 (2008) 5758.

TF-ThP12 Ultra High Rate Depositions of Various Transparent Conductive Oxide Films of AZO, ITO and ATO by Reactive Magnetron Sputtering*, Y. Nishi, **K. Hirohata**, Y. Muto, Y. Kawase, N. Tsukamoto, N. Oka, Y. Sato,* Aoyama Gakuin University, Japan*, Y. Iwabuchi, H. Kotsubo,* Bridgestone Co., Japan*, Y. Shigesato*, Aoyama Gakuin University, Japan

Transparent conductive oxide (TCO) is a highly degenerated wide band-gap semiconductor with low electrical resistivity and high transparency in the visible and near-infrared regions. In this study we will report the very high rate deposition of various TCOs, such as Al-doped ZnO (AZO), Sn-doped In_2O_3 (ITO) or Sb-doped SnO_2 (ATO) films by reactive sputtering using Zn-Al, In-Sn or Sn-Sb alloy targets, respectively.

In general the deposition rate for the sputtering using the oxide ceramic targets is not so high and also the cost for the high quality ceramic targets is high. On the other hand, reactive sputtering using the alloy targets should be one of the most promising techniques to achieve much higher deposition rate for various industrial applications because sputtering yield of the metallic surface is much larger than oxide surface and also the higher sputtering power density can be applied for metallic targets with the higher thermal conductivity. The reactive sputtering process, however, is strongly affected by the O_2 flow ratio; the deposition rate exhibits hysteresis with respect to the O_2 reactive gas flow rate. Such behavior originates in the oxidation state of the target surface, resulting in the marked decrease in deposition rate with the increasing O_2 flow. Therefore, the sputtering conditions should be precisely controlled so as to obtain high-quality TCO films by reactive sputtering processes with a high deposition rate and with high reproducibility. In order for the precisely controlled deposition a specially designed feedback system (Fraunhofer Institut fur Elektronenstrahl-und Plasmatechnik, FEP) of discharge impedance or plasma emission intensity combined with mid-frequency (mf, 50 kHz) pulsing has been carried out [1-5] . Oxidation of the target surface was precisely controlled by these feedback systems in the "transition region", where the deposition rate and the stoichiometry . The deposition rate was about 10-20 times higher than the one deposited by conventional sputtering depositions using oxide ceramic targets.

[1] M. Kon, Y. Shigesato, et al., Jpn. J. A ppl. Phys. 41, (2002) 814.

[2] M.Kon, Y. Shigesato, et al., Jpn.J. Appl. Phys., Vol.42, No.1, (2003) 263.

[3] S. Ohno, Y. Shigesato, et al., Jpn. J. Appl. Phys., Vol. 43, No.12 (2004) 8234.

[4] S. Ohno, Y. Shigesato, et al., Thin Solid Films 496 (2006) 126.

[5] S. Ohno, Y. Shigesato, et al., Science and Technology of Advanced Materials 7 (2006) 56.

TF-ThP13 Electrical Resistivity Change of Al:ZnO Thin Films Dynamically Deposited by Bipolar Pulsed DC Sputtering with a Remote Plasma Source*, **W. Yang**, J. Joo*, Kunsan National University, Republic of Korea

Bipolar pulsed DC magnetron sputtering is used to deposit Al-doped ZnO (AZO) for a transparent conducting oxide in a solar cell structure. A 5-inch × 25-inch AZO target was sputtered by a bipolar pulsed DC power supply to deposit AZO thin films on a 400-mm × 400-mm glass substrate by swinging it back and forth over a cathode. Because of this dynamic deposition process, a zigzagged columnar structure observed. It decreased electrical resistivity. To recover the disadvantage, a remote plasma source (RPS) was used to give more mobility to adatoms, resulting in lowered resistivity. However, it increased from 2.11×10^{-3} W·cm to 2.30×10^{-3} W·cm as the power of remote plasma source was increased over some threshold value. By using RPS, the deposition rate decreased, but we expect that the resistivity becomes better because the additional ions may disturb the formation of a zigzag-type column structure. In this paper, we will address how the RPS affects the resistivity of the AZO thin films during the dynamic deposition process by plasma characterizations and microstructure analysis.

TF-ThP14 Photo-functional Properties of TiO_2/W-TiO_2/TiO_2 Films Prepared by Reactive Magnetron Sputtering*, **H. Shukur**, K. Komiyama, M. Sato, I. Takano*, Kogakuin University, Japan

TiO_2 as photo-functional material is one of lower cost material and harmless material to environment. It is expected to use as material of clean energy in future. Furthermore the photocatalytic property provides antibacterial or antifouling effect. These effects decompose environmental pollution matters (like nitrogen oxide etc.) by generate active oxygen (O^{2-}, OH), when TiO_2 is exposed to sunlight. On the other hand, TiO_2 has characteristically electrical properties such as an n-type semiconductor or a dielectric. In order to improve the electrical and photocatalytic property of TiO_2, many researchers have used various methods such as gas or metal doping into TiO_2 techniques etc. In this study, tungsten (W) was doped to TiO_2 thin film to improve the electrical properties and to enhance the photo-sensitivity of TiO_2 thin film. The doping of W in TiO_2 thin film generates tungsten oxide (WO_3) and this oxide shifts the conduction band of TiO_2 to the positive side because of the low band gap of WO_3 (2.8eV) as compared with that of TiO_2 (3.2eV). As a result, because the motion energy of each electron becomes smaller, excited electrons in a visible region (wavelength more than 400 nm) increase and promote the photocatalytic reaction in this region.

TiO_2 thin films were prepared by using the reactive magnetron sputtering method on stainless steel substrate (SUS304) of 18×18 mm in size and also glass substrate of 18×9 mm in size. All samples were formed in four layers. The first one was a Ti layer with 50 nm in thickness. The second layer was a TiO_2 layer of 170 nm. The third layer and surface layer were W-doped TiO_2 of 30 nm and TiO_2 of 10 - 60 nm, respectively. Other formation conditions were 1.1 sccm in O_2 gas flow rate and 20 sccm in Ar gas flow rate. Ti and W sputtering rate were fixed at 0.025 nm/sec and 0.002nm/sec, respectively. The substrate temperature through this formation process was set at 200 °C.

The photocatalytic property was measured by a methylene blue immersion test. The difference in light absorbance at a wave length of 665 nm after light irradiation for 12 hours using sterilization, fluorescent and an artificial sunlight lamp (with UV band filter) was measured by a spectrophotometer (SHIMADZU UV-2550). Photoelectric current was measured by a cyclic volt ammeter system.

The photo-functional properties of W-doped TiO_2 were improved by the additional TiO_2 onto the W-doped TiO_2 layer. Photocatalytic property showed a higher value under artificial sunlight irradiation when the surface layer thickness was 20 nm.

TF-ThP15 Resistivity Characteristics of Transparent Conducting Impurity-doped ZnO Films for Use in Oxidizing Environments at High Temperatures, ***J. Nomoto***, *M. Konagai, T. Miyata, T. Minami*, Kanazawa Institute of Technology, Japan

For the purpose of determining the most suitable material to use as transparent electrodes in thin-film solar cells, this paper compares in detail the resistivity behavior of transparent conducting Al-doped ZnO (AZO) and Ga-doped ZnO (GZO) thin films for use in oxidizing environments at high temperatures. These thin films with thicknesses in the range from approximately 100 to 3000 nm were prepared on glass substrates at a temperature of 200°C by either an rf superimposed dc or a conventional dc magnetron sputtering deposition (rf+dc-MSD or dc-MSD). The obtained resistivities in AZO and GZO thin films prepared by rf+dc-MSD were always lower than those in films prepared by dc-MSD. However, the obtainable resistivity of the thin films prepared by an rf+dc-MSD using lower resistivity targets was not decreased more sufficient than that of thin films prepared by a conventional dc-MSD with the same targets, whereas the obtained resistivity decreased as the resistivity of targets used was decreased. In moisture-resistant tests, resistivity change was measured over time with exposure to a highly moist environment (air at 85% relative humidity and 85°C). The resistivity stability of GZO thin films over long term testing was found to be always lower than that of AZO thin films prepared with the same thickness under the same deposition conditions. In heat-resistance tests, resistivity was measured both before and after heat treatment in an oxidizing atmosphere (30 min. in air at a temperature up to 400°C). The resistivity stability of AZO thin films during heat testing at 400°C was found to be always lower than that of GZO thin films prepared with the same thickness under the same deposition conditions. It was also found that the increase of resistivity observed in AZO films was related to decreases of both the carrier concentration and the Hall mobility, but, in contrast, that observed in GZO films was mainly attributable to a decrease of carrier concentration. The difference of resistivity behavior in the heat tests was mainly attributed to the micro-structural difference associated with the crystallinity of deposited films.

TF-ThP16 Effect of DC bias on the Characteristics of Low Temperature Silicon-Nitride Films Deposited by Internal Linear Inductively Coupled Plasma Source, ***G.H. Gweon***, *J.H. Lim, S.P. Hong, G.Y. Yeom*, Sungkyunkwan University, Korea

There has been a growing interest in the dielectric material that can be deposited at low substrate temperatures for the applications such as organic devices and flexible display devices. Of diverse dielectric materials, silicon-nitride film has been widely used for various important applications from semiconductor to flat panel display, such as a gate dielectric material for thin film transistor (TFT), passivation layers for diverse microelectronics and as anti-reflection (AR) coating for solar cell. In addition, due to their chemical inertness, excellent dielectric properties, and thermal stability compared with those of silicon oxide, many researchers have been studied to develop high quality low temperature silicon-nitride films using various types of plasma sources. Generally, conventional technique for depositing SiN at a low temperature is plasma-Enhanced CVD (PECVD) (~300℃).

In this study, we carried out the deposition of silicon nitride thin films at the temperature lower than 100℃ by using an internal linear ICP source. To obtain high quality silicon-nitride films, the effects of the ratio of NH_3 to SiH_4 and DC bias on the properties of thin film were investigated. The results showed that, by using 2:1 ratio of NH_3:SiH, and by using -150V DC bias, the high quality silicon nitride film having the refractive index of 1.83, dielectric constant of 7.2 with negligible interface traps could be observed. The compositions, binding states, and the refractive indices of the films were measured using a XPS, FTIR, and an ellipsometer, respectively. In addition, metal/insulator/semiconductor (MIS) capacitors having Al/insulator/p-Si were fabricated and the flat-band voltage and hysteresis voltage were measured by the capacitance-voltage (C-V) method.

TF-ThP17 Characterization of Structural Modification in Columnar Thin Films produced by Ion-Assisted Glancing Angle Deposition, ***J.B. Sorge***, University of Alberta, Canada, *M.J. Brett*, NRC National Institute for Nanotechnology, Canada

In a traditional glancing angle deposition (GLAD) process, the column tilt angle β and film density ρ are both governed by the deposition angle α. It was later discovered that β could be controlled independently from the deposition angle by implementing an appropriately designed phisweep substrate rotation algorithm which reduces anisotropic shadowing[1]. Ion-assisted deposition has also been demonstrated to alter columnar thin film morphology[2] which has proven to be useful in humidity sensing applications[3]. The influence of the phisweep process on β is inherently limited to producing tilt angles that are less than or equal to that of a traditional GLAD film grown without phisweep. Ion assisted GLAD is a procedure that can increase β above the maximum achievable tilt angle in a standard GLAD deposition and has been utilized in square spiral photonic crystal fabrication[4]. The work reported here is a fundamental study of SiO_2 columnar thin films grown with an ion-beam assisted GLAD process. Our current capabilities in modifying β as a function of α with an ion assisted process will be described. In addition, we report on our efforts to decouple the film density ρ from α; a previously unstudied characteristic of the ion assisted GLAD process. This latter result could enable partial decoupling of α, β and ρ simultaneously and allow access to previously unattainable columnar film morphologies, improving the versatility of the GLAD process. Discussion will focus on the effect of ion assistance on ρ and β as measured by variable angle spectroscopic ellipsometry (VASE) and the influence of different α. The relationship between these parameters, the natural column broadening and effects on the resulting in-plane birefringence will also be discussed.

[1] M. O. Jensen, and M. J. Brett, *Appl. Phys. A*, **80**, 763 (2005)

[2] I. Hodgkinson, and Q.H. Wu, *Mod. Phys. Lett. B*, **15**, 1328 (2001)

[3] M.T. Taschuk, J.B. Sorge, J.J. Steele, and M.J. Brett, *IEEE Sensors Journal*, **8**, 1521 (2008)

[4] J.B. Sorge, M. A. Summers, M. D. Fleischauer, K. Tabunshchyk, A. Kovalenko, and M. J. Brett, *Mat. Res. Soc. Sym. Proc.*, **1014E**, 1014-AA07-26 (2007)

TF-ThP18 Structural and Electrical Characterization of rf Magnetron Sputtered Aluminum Doped Zinc Oxide, ***K. Braam***, *M. Kyslinger, J. Doyle*, Macalester College

We present a study of the relationship between structural properties and opto-electronic quality of aluminum doped zinc oxide produced by rf magnetron sputtering. Thin films (300-400 nm thick) were deposited as a function of substrate temperature, working gas (argon) pressure, and oxygen partial pressure. Structural measurements included x-ray diffraction, scanning electron microscopy, Raman spectroscopy, and infrared spectroscopy. Electrical measurements included resistivity, Hall effect, and optical transmission. Substrate temperature had a strong effect on the crystalline quality of the films as inferred from xrd, infrared, and Raman measurements. Working gas pressure and oxygen partial pressure had a much weaker effect on the crystal structure. Good opto-electronic properties were not always correlated with good crystal quality. In particular good electronic quality films could be produced under deposition conditions that resulted in poor crystal quality. A simple model is presented that relates the crystal quality to the electronic properties accounting for dopant activation, grain boundary scattering, and ionized impurity scattering.

TF-ThP19 Effect of Silicon Content on the Resistivity of Tungsten Silicon Film, ***C. Lo***, *D. Draper, P. McDonald, R. Mathew*, Praxair Electronics

Tungsten (W) –silicon (Si) alloy has been used for many applications in the semiconductor. Resistance layer is one of the applications. In this study, five sputtering targets with composition ranged from WSi1.6 (W- 20wt% Si) to WSi4 (W- 38wt% Si) have been prepared. By controlling the sputtering power and Argon (Ar) gas pressure, the film resistivity as a function of target composition and sputtering parameters has been established. The results are able to provide helpful information to the alloy design of WSi for new thin film applications.

TF-ThP20 Effect of Process Parameters on the Growth and Properties of ATO Films Prepared on Flexible Substrate at Room Temperature, *S.U. Lee*, *B.Y. Hong*, Sungkyunkwan University, Korea

Transparent conducting oxide (TCO) have found applications in several optoelectronic devices such as light emitting diodes (LEDs), solar cells, and flat panels as well as flexible displays, due to their excellent electrical and optical properties. In general, of all TCO films, glass is the most commonly selected substrate. However, for future development in flexible devices, glass is limited by its intrinsic inflexibility, thickness and weight characteristics. The objective of this study was to characterize the electrical, structural and optical properties of antimony-doped tin oxide (ATO) films prepared on a polyethersulfone (PES) flexible substrate by the radio frequency (RF) magnetron sputtering method for applications to transparent electrodes using a SnO_2 target mixed with Sb of 6 wt% at room temperature. The process parameters were working pressure and RF power. The working pressure was varied from 1 to 7 mTorr in steps of 2 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 was calculated from the XRD spectra using the Scherrer equation. The change in FWHM reflects the change in the grain size of the film, that is, the decrease in FWHM corresponds to the increase in grain size. ATO film deposited on PES substrate at optimized condition showed the lowest resistivity of 7.4 $x10^{-3}$ ohm-cm and the optical transmittance was 85% in the visible range. The possibility as the next-generation transparent electrode is also studied.

TF-ThP21 Development of a Transparent Barrier Layer for CdTe Thin Film Solar Cells Deposited on Flexible Foil Substrates, ***D.R. Hodges***, *V. Palekis, E. Stefanakos, C.S. Ferekides*, University of South Florida

Cadmium telluride (CdTe) is a leading thin film photovoltaic (PV) material due to its near ideal band gap of 1.45 eV, its high optical absorption coefficient and availability of a various device fabrication methods. The status the thin film CdTe solar cell is more than 16.5% efficiency for devices on conducting glass substrates and 7.8% efficiency for devices on flexible metallic substrates. Thin stainless steel (SS) foils are used as the substrate for the development of CdTe solar cells because of its material properties, high temperature stability, commercial availability and cost. A potential problem with the use of a stainless steel foil as the substrate is the diffusion of iron (Fe), chromium (Cr) and other elemental impurities into the layers of the solar cell device structure during high temperature processing. A diffusion barrier limiting the out diffusion of these substrate elements is being investigated in this study. Silicon nitride (Si_3N_4) films deposited on SS foils are being investigated as the transparent barrier layer, to reduce or inhibit the diffusion of substrate impurities into the solar cell. Si_3N_4 coefficient of thermal expansion (CTE) of $4.5x10^{-6}$/°K is close to both the back contact layer Molybdenum, with a CTE of $5.1x10^{-6}$/°K and the absorber CdTe, with a CTE of $5.9x10^{-6}$/°K, minimizing thermal expansion mismatch in the device. It has already been shown by others, that substrate impurities like Fe and Cr in the cell's absorber can lead to reduced cell efficiencies. In this study, the effect of the Si_3N_4 barrier layer is being evaluated for its effect on cell efficiency and overall device performance. The optimum Si_3N_4 barrier thickness is also being determined. Currently thin film CdTe cells are being fabricated with and without a Si_3N_4 barrier layer. Preliminary results show an improvement in the V_{OC} of cells fabricated with a 0.1 µm thick Si_3N_4 barrier layer. The thin film CdTe solar cells have been characterized by XRD, SEM, Secondary Ion Mass Spectrometry (SIMS) depth profiles, current-voltage (I-V) characteristics and spectral response.

TF-ThP22 Design and Fabrication of Optical Thin Films for Remote Sensing Instrument, ***C.N. Hsiao***, *H.P. Chen, P.K. Chiu, W.H. Cho, Y.W. Lin,* National Applied Research Laboratories, Taiwan, *D.P. Tsai*, National Applied Research Laboratories and National Taiwan University

Optical thin films of Ag mirror and band pass filters were design and deposited on radiation-resistance glass by ion beam assisted deposition for the use of optical payload in remote sensing instrument. Optical parameters were optimized by the admittance loci analysis to show that the mirror and filters can achieve average reflectance of 99 % in visible spectrum and average transmittances of 95 % in the spectral range of blue, green, red, NIR and pan chromatic, respectively. The corresponding properties of films were investigated by in-situ optical monitoring, spectrometer, ellipsometry and high resolution transmission electron microscopy (HRTEM). It was found that the average reflectance of Ag mirror(with protect coating) is above 98 %. The average transmittances are above 85 % for all the five band pass filters, with the rejection transmittance lower than 1% in the spectral range of 350~1100 nm. Furthermore, in order to determinate the optical stability of optical thin films for aerospace applications, space environmental test was simulated by using a Co^{60} gamma (g) radiation source (total dose of 35 krad and 1 Mrad). The optical stability of the films with the radiation test will be discussed.

TF-ThP23 Effect of Vacuum Annealing on Charge Transport and Trapping in a-SiC:H/c-Si Heterostructures, *A. Nazarov, I. Tatarchuk, Y. Gomeniyuk, A. Vasin, A. Rusavskii, V. Stepanov, V. Lysenko,* NASU, Ukraine, ***S. Ashok***, The Pennsylvania State University

a-$Si_{1-X}C_X$:H alloys are of interest in detectors and white light emitting devices, but their properties under thermal anneal have not been reported so far. This paper considers the processes of charge transfer and trapping in a-$Si_{1-X}C_X$:H films deposited on crystalline p-type Si wafers and annealed in vacuum (10^{-6} Torr) over temperature range of 300 to 850°C. The a-$Si_{1-X}C_X$:H films were deposited by reactive magnetron sputtering using of the Ar /CH_4 as working gases. An Au/Ti multilayer was used as a contact to the a-$Si_{1-X}C_X$:H film and Al as back contact to the Si wafer. Raman scattering spectroscopy, photoluminescence (PL) spectroscopy and electron paramagnetic resonance (EPR) measurements were carried out at room temperature. Current-voltage (I-V) and capacitance-voltage characteristics were measured in the temperature range 100 - 350K.

Evaluation of the I-V characteristics of the initial structure and the structures annealed at 450 °C and 650°C demonstrates that maximum coefficient of rectification is observed for the heterostructure annealed at 450°C and equals $4x10^2$ for ±5V. For this material the maximum optical band gap and minimum paramagnetic defect concentration are observed. The dielectric constant is found to be 6.5. After 650°C vacuum annealing the forward and reverse currents are higher than those of both the initial and 450°C- annealed structures, and are associated with amorphous carbon cluster formation observed by Raman scattering after such thermal annealing. Temperature dependence of forward current of the initial structure demonstrates that variable-range hopping (VRH) conductivity at the Fermi level is dominant up to 1V. The density of states at the Fermi level is estimated at $\sim 8x10^{19}$ $cm^{-3}eV^{-1}$, that is on the order of the concentration of Si and C dangling bonds, determined by EPR technique. Increase of the forward voltage from 0.1V to 1.0V results in increase of average hopping distance from 4.2 nm to 7 nm. Annealing at 450°C results in change of current transport mechanism: now the forward current can be described by Pool-Frenkel emission from levels with energy ~ 0.11 eV. Annealing at 650°C considerably reduces the temperature dependence of current, testifying to the emergence of tunneling processes for charge movement. The process of VRH conductivity through a large density of state at Fermi level again appears, with an estimated density of the states around $5x10^{20}$ $cm^{-3}eV^{-1}$. Increase of applied voltage beyond |1V| results in a decrease in current with increase of temperature. It is surmised that the observed phenomenon is associated with charge trapping in local regions separated from main matrix by high potential barriers.

TF-ThP24 Photoelectron Emission Properties and Work Function of Sn-doped In_2O_3 Films, ***A. Takasaki***, *Y. Sato, N. Oka,* Aoyama Gakuin University, Japan, *F. Utsuno, K. Yano,* Idemitsu Kosan Co., Ltd., Japan, *Y. Shigesato*, Aoyama Gakuin University, Japan

Sn-doped In_2O_3 (ITO) film has been used as a transparent electrode for various applications including organic light-emitting diodes (OLEDs) since it combines good conductivity and transparency in the visible region. The work function control of ITO film plays an important role in device parameters such as operation voltage or lifetime for OLED. The work function of ITO film has been controlled by surface treatments by plasma or UV-ozone treatment. However in such methods the work function of ITO film is unstable and can change over time. On the other hand, it is expected that the work function could be controlled by a variation in carrier density. In this study, we investigate how the work function depends on the carrier density of ITO films. The ITO films with various carrier densities were deposited by dc magnetron sputtering on glass substrates heated at 300 °C and 400 °C using high-density ceramic ITO targets with various SnO_2 concentrations. Total gas pressure and dc power were maintained at 1.0 Pa and 50 W, respectively, for all the depositions. The film thickness of all the ITO films was adjusted as about 200 nm. Carrier density was controlled from 3.06×10^{19}-5.72×10^{20} cm^{-3} or 4.42×10^{19}-1.08×10^{21} cm^{-3} for the films deposited on the substrates heated at 300 °C or 400 °C, respectively, by using the ceramic ITO targets with the different SnO_2 concentrations from 0 to 10 wt. %. The increase in the carrier density should be caused by the increase in the substitutional Sn^{4+} at In^{3+} sites of In_2O_3. Optical band gap of the films increased with the increasing SnO_2 concentration of the target, where work function decreased. This must be explained quantitatively in terms of the shift of Fermi level with varying carrier density within a parabolic conduction band. The optical band gap or the work function of the films showed clearly positive or negative relationships to the two-thirds power of carrier density, respectively. Furthermore, a detailed analysis was performed using hard X-ray photoemission spectroscopy (HX-PES) in order to investigate the electronic state between the Fermi level and the valence band of ITO films deposited on the substrates heated at 400 °C. As a result, the density of state near the Fermi level was found to vary systematically with the carrier density. The synchrotron radiation experiments were performed at the BL47XU in the SPring-8 with the approval of the Japan Synchrotron Radiation Research Institute (JASRI) (Proposal No.2009A1586).

TF-ThP25 Enhanced Light-Emission Characteristics and Analyses of Electronic Band Structure of 2-TNATA / MoO_x for an Efficient Hole-Injection in Organic Light-Emitting Diodes

J.W. Kwon, *J.T. Lim, G.Y. Yeom*, Sungkyunkwan University, Korea

Recently, the studies on metal-organic interfaces are concentrated in the efficient charge carrier-injection between electrodes and an adjacent organic layer adjoining to electrodes. The efficient carrier-injection properties are very important for improving a luminace and luminous efficiency in the field of the information display such as the organic light-emitting diodes, organic solar cells, organic thin film transistor, and organic sensors, and organic smart window devices. Here, we reported on the new hole-only contact system of 2-TNATA / MoO_x. The organic light-emitting diode with a glass / ITO (85 nm) / MoO_x (5 nm) / 2-TNATA (30 nm) / NPB (18 nm) / Alq_3 (52 nm) / LiF (1 nm)/Al (100 nm) structure showed higher luminous efficiency as two times than the device of the same structure with MoO_x of 0 nm-thick. The improvement of the luminous efficiency by inserting a MoO_x layer between tin-doped indium oxide (ITO) and 2-TNATA is attributed to the lowing of the barrier height in a hole injection ($\Phi_B{}^h$) as well as the raising the band banding by pinning of Fermi level in the interfaces between two layers. The mechanism for a hole-injecting efficiency from anode to a MoO_x / 2-TNATA layer was proved by analyzing an ultraviolet photoemission spectroscopy (UPS) spectra. $\Phi_B{}^h$ in the 2-TNATA / MoO_x interface with MoO_x of 20 nm-thick was decreased about 2.0 eV, when compared to $\Phi_B{}^h$ of the pure layer with only 2-TNATA.

Keywords: organic light-emitting diode, electronic structure, interface, MoOx, 2-TNATA

TF-ThP26 Unusual Properties of InN Epilayers Probed by Photoluminescence

F.I. Lai, ***W.T. Lin,*** Yuan-Ze University, Taiwan, *W.-C. Chen, C.N. Hsiao,* National Applied Research Laboratories, Taiwan, *S.Y. Kuo,* Chang Gung University, Taiwan, *Y.K. Liu, J.L. Shen*, Chung Yuan Christian University, Taiwan

In this paper, we report the studies on the hetero-epitaxial growth of wurtzite indium nitride (InN) thin films on oxide buffer layer by plasma-assisted chemical beam epitaxy (CBE) system with different III/V ratios. Oxide buffer layer was pre-sputtered using RF sputtering technique before InN deposition. The structural and optical properties of InN films samples were investigated by x-ray diffraction (XRD), field-emission scanning electron microscopy (FE-SEM) and temperature-dependence photoluminescence (PL) measurements. The near-infrared emission peak values of samples were between 0.74 and 0.78 eV, which are higher than those pre-reported values explained by the Moss-Burstein effect. While increasing the III/V ratio, the emission PL peak red-shifted. In addition, the temperature-dependence PL spectra exhibit blue-shifted as the measurement temperature increased. We suggest that the blue shift in PL spectra with temperature may result from the variation in concentration of InN films.

TF-ThP27 Thermophysical Properties of Alq_3 and α-NPD Films Measured by Nanosecond Thermoreflectance Technique

N. Oka, ***K. Kato***, Aoyama Gakuin University, Japan, *N. Ito*, Panasonic Electric Works Co., Ltd., Japan, *T. Yagi, N. Taketoshi, T. Baba,* National Metrology Institute of Japan, AIST, Japan, *Y. Sato, Y. Shigesato*, Aoyama Gakuin University, Japan

Organic light-emitting diodes (OLEDs) are promising for future lighting and display applications. It has been reported, however, that the electroluminescence properties are degraded by self-heating during operation [1,2]. In order to determine the heat propagation mechanism in OLEDs, it is important to measure the thermophysical properties precisely for the components of OLEDs, such as Tris-(8-hydroxyquinoline) aluminum (Alq_3) and N,N'-Di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) films. Alq_3 and α-NPD are used as the electron-transport/emitting materials and the hole-transport material, respectively. In this study, thermal diffusivity of both the films was characterized quantitatively by ‘rear heating / front detection (RF) type’ nanosecond thermoreflectance systems [3] (NanoTR, PicoTherm), which can directly observe the heat propagation through the film thickness. Alq_3 and α-NPD films sandwiched between aluminum films (Al/Alq_3/Al, Al/α-NPD/Al) were prepared on alkali-free glass substrates by means of vacuum evaporation . The nominal thicknesses of Al, Alq_3 and α-NPD layer were respectively 100 nm, 50-200 nm and 100 nm. The thermal diffusivity of Alq_3 films was found to be $1.4\text{-}1.6\times10^{-7}$ m^2/s, which is about 1.5 times higher than that of Alq_3 powder [4]. Furthermore, the thermal diffusivity of α-NPD films is 1.2×10^{-7} m^2/s. We also estimated the mean free path of phonons, l_{ph}, in terms of phonon propagation in Alq_3 films using the thermal conductivity calculated from the thermal diffusivity, heat capacity per unit volume, and the average phonon velocity calculated from Young’s modulus and the density [5]. As a result, l_{ph} was approximately 0.49 nm, which is smaller than molecular size and intermolecular distance for Alq_3, but almost twice the Al-N bond length [6,7].

<Acknowledgment>

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) as a project of "Development of High-efficiency Lighting Based on the Organic Light-emitting Mechanism".

[1] T. Sugiyama, H. Tsuji, Y. Furukawa, Chem.Phys.Lett. **453** 238 (2008).

[2] G. Vamvounis, H. Aziz, N. Hu, Z. Popovic, Synthetic Metals **143** 69 (2004).

[3] T. Baba, Proc. 10th International Workshop on Thermal Investigations of ICs and Systems, Sophia Antipolis, France 241 (2004).

[4] M. W. Shin, H. C. Lee, K. S. Kim, S. H. Lee, J. C. Kim, Thin solid Films **363** 244 (2000).

[5] C. Kittel, Introduction to Solid State Physics, 7th ed., Wiley, New York (1996).

[6] H. S. Karlsson, K. Read, R. Haight, J. Vac. Sci. Technol. A **20(3)** 762 (2002).

[7] A. Curioni, M. Boero, W. Andreoni, Chem. Phys. Lett. **294** 263 (1998).

TF-ThP28 Characterization of the Defects in Intrinsic Nanocrystalline Silicon Thin Films Deposited by an Internal-ICP

H.C. Lee, *I.K. Kim, G.Y. Yeom*, Sungkyunkwan University, Korea

Nano-, microcrystalline hydrogenated silicon(nc-, μc-Si:H) attracts much interest as a promising material for thin film solar cells with high performance and good stability compared to amorphous silicon thin film. The deposition of nc-, μc-Si:H has been carried out by using various methods such as hot-wire chemical-vapor deposition (HWCVD), photo-chemical vapor deposition (P-CVD), plasma-enhanced chemical-vapor deposition (PECVD), etc.

During the deposition of nano- micro- crystalline hydrogenated silicon, the defects are generated and the defects in the nanocrystalline silicon thin films can degrade the efficiency of the solar cell. Defects located at deep-gap or tail states in the disordered silicon films are of great importance for the electronic quality of these materials and these states will influence the performance of the solar cells.

In this study, we have investigated the defects in the nancrystalline silicon thin film as a function of crystallization of the nanocrystalline silicon thin film. The nanocrystalline silicon thin film was deposited by using an internal-type inductively coupled plasma system. Electron spin resonance (ESR) is a useful tool for the investigation of defects in amorphous, nano-, and micro- crystalline hydrogenated silcon thin film. The nanocrystalline silicon thin films were deposited on corning 1737 glass. Raman scattering spectroscopy, high resolution transmission electron microscopy, (HRTEM) and electron spin resonance(ESR) were used to evaluate film crystallinity, structural image, and defects in the film, respectively.

TF-ThP29 Damages to Fatigue and Retention Characteristics of BLT Capacitors Fabricated by Damascene Process with High-pressure Process

W Lee, *S Shin,* Chosun University, Korea, *N. Kim*, Chonnam National University, Korea

Damascene process of chemical mechanical polishing (CMP) process was proposed to fabricate the BLT ferroelectric capacitor instead of plasma etching process for the vertical profile without plasma damage. However, the authors also reported in the previous study that the electrical damages to leakage current and *P-V* characteristics of BLT capacitor induced by high-pressure process of damascene process although the high-pressure process had shown the better removal rate (high yield) and the sufficient surface characteristics including non-uniformity for BLT-CMP [1,2]. BLT thin films deposited on $Pt/Ti/SiO_2/Si$ substrate is well known to have good fatigue endurance and retention characteristics; however, the high-pressure process in damascene process of BLT degraded the fatigue behavior and retention characteristics. Therefore, the CMP pressure was controlled in damascene process for BLT capacitor although the yield and the surface characteristics became somewhat lower. Fatigue behavior and retention characteristics of BLT capacitor were recovered with the good *P-V* and leakage current characteristics. [1] N.-H. Kim, *et al.*, Thin Solid Films, Vol.

515, Iss. 16, p. 6456 (2007), [2] N.-H. Kim, *et al.*, Electronics Letters, Vol. 44, Iss. 24, p. 1429 (2008).

TF-ThP30 Surface Roughening of ZnO Films by Atomic Layer Deposition, ***F.C. Hsieh**, M.Y. Tsai, C.C. Kei, C.C. Yu, W.H. Cho, C.Y. Su, C.S. Yu, D.R. Liu, C.N. Hsiao*, National Applied Research Laboratories, Taiwan, Republic of China

ZnO films were deposited by atomic layer deposition (ALD) on glass at 40°C. The films were studied by Atomic force microscope (AFM), X-ray diffraction (XRD), and contact angle measurements. The root mean square (RMS) roughness of ZnO increases with increasing the number of growth cycles. According to the XRD analysis, the crystalline phase becomes apparent when the growth cycle is increased. The contact angle decreases substantially at 400 cycles and the film reveals rough hydrophilic. The surface roughening of ZnO films can be turned by the growth cycle at this lower temperature due to the presence of ZnO nanocrystals.

TF-ThP31 Glancing Angle Deposited Metallic Nano-Structured Thin Films for Surface Enhanced Fluorescence and Biosensing in Water*, C. Khare,* Leibniz-Institut of Surface Modification, Germany*,* ***A. Karabchevsky**, I. Abdulhalim,* Ben Gurion University of the Negev, Israel*, C. Patzig,* Leibniz-Institut of Surface Modification, Germany*, B. Fuhrmann,* Martin-Luther-University Halle, Germany*, B. Rauschenbach*, Leibniz-Institut of Surface Modification, Germany

Metallic nanophotonic structures demonstrate surfaced enhanced phenomena, thus find their application in device photonics. To facilitate the improvement in the already successful panoply of optical biosensors in general and in the field of water quality in particular, nano-photonic structures such as sculptured thin films (STF) can be used. The existence of localized surface plasmon resonance (LSPR) was observed within metallic STFs. The glancing angle deposition technique (GLAD) by ion beam sputtering and electron beam evaporation was employed to sculpt thin films as a platform for surface enhanced fluorescence (SEF). The self shadowing mechanism is responsible for the growth of non-closed films which consist of needles grown in the direction of the incoming flux of the particles. This thin film deposition method, coupled with an appropriate substrate rotation scheme, enabled to deposit nanorods with less than 30° and greater than 80° inclination with respect to the substrate surface. A multitude of structures were prepared by depositing materials like Ag, Au and Si with GLAD on different substrates such as fused silica, Si(100), Si(100) coated with 15 nm Ti, and on nanosphere lithography pre-patterned substrates that consist of Au and Al nanodots in hexagonal arrangement. The reference (compact) thin films of each material were prepared with the vapor incidence parallel to the substrate normal.

With the integration of a fluorescence microscope with a spectrometer, the green Hg line at 546 nm was used for excitation in most of the SEF experiments and the emission was detected using the red filter at 590 nm. STFs spin coated with a Rhodamine 123 layer of thickness (30-50) nm were observed to show enhancement factors up to few tens. A higher degree of surface enhancement was observed with Ag nanorod STFs inserted in an aqueous solution of *E. coli* in comparison to corresponding dense Ag reference film.

TF-ThP33 Molecular Layer Deposition of Organic Films for EUV Photoresists, ***H. Zhou**, P.W. Loscutoff, S.F. Bent*, Stanford University

Lithography at the sub-22 nm length scale will require resist films under 50nm thick with a high degree of homogeneity. Current resists that are in use for ultraviolet lithography may not be suitable for the projected transition to extreme ultraviolet (EUV) wavelengths, leading to active study of alternative materials solutions. One method for gaining sub-nanometer control over the thickness and composition of photoresist film is molecular layer deposition (MLD), which utilizes a series of self-limiting reactions of organic molecules. In this study, a variety of nanoscale organic films were deposited by MLD via urea coupling chemistry, which occurs by reaction of isocyanates and amines. Films were deposited on substrates that were first prepared by vapor deposition of 3-aminopropyltriethoxysilane on hydroxylated SiO$_2$ surfaces to yield an amine-terminated surface, as confirmed by ellipsometry and XPS. Following amine termination, the diisocyanate and diamine precursors were dosed in a binary cycle, and this cycling was repeated to yield the desired thickness of organic film. Ellipsometry indicates a linear growth rate of 4.5 Å/cycle for the standard coupling of phenylene diisocyanate (PDIC) and ethylenediamine (ED). The urea coupling moiety is confirmed by infrared spectroscopy, and films are shown to have stoichiometric composition by XPS. Temperature dependent measurements show that the films have good thermal stability. To fabricate EUV resists, we have explored a variety of backbones contained within the amine and isocyanate linking groups to tune the functions of the organic films. By changing the backbone of the MLD precursors, we have incorporated ketal-based acid-labile groups into the film and have shown that after incorporation of photoacid generator (PAG), UV exposure, post-exposure bake and development, the films are cleaved, leading to potential use as photoresists. Results of applying the nanoscale oligourea films for advanced photoresist application will be presented.

TF-ThP34 Time-Resolved FTIR Spectroscopy During ALD*,* ***B.A. Sperling**, J.E. Maslar, W.A. Kimes, D.R. Burgess, Jr., E.F. Moore*, National Institute of Standards and Technology

In situ monitoring of atomic layer deposition (ALD) could potentially make process optimization faster and more cost-efficient. Additionally, it permits computational models for chemistry and fluid dynamics to be tested and refined; these validated models, in turn, could also be useful tools for process development and equipment design. We have been developing real-time diagnostics for gas-phase concentrations using a number of methods including mass spectroscopy, distributed-feedback diode laser absorption spectroscopy, and quantum cascade laser absorption spectroscopy. This work focuses on our work with time-resolved Fourier transform infrared (FTIR) spectroscopy, which we use to monitor gas-phase species during ALD of hafnium oxide from tetrakis(ethylmethylamino) hafnium and water. Results are compared to other measurement techniques applied to the same warm-walled, single-wafer reactor. Additionally, our efforts to model the system using computational fluid dynamics and a detailed kinetic reaction mechanism are discussed.

TF-ThP35 Characteristics of Thin Films Deposition of Ruthenium on Various SiO$_2$ Substrates by Remote Plasma Atomic Layer Deposition, ***J.S. Lee**, T.Y. Park, D.O. Kim, H.T. Jeon,* Hanyang University, Republic of Korea*, K.H. Lee, B.C. Cho,* IPS R&D Center, Korea*, M.S. Kim, H.B. Ahn*, Air Product Korea

High-k dielectrics, such as HfO$_2$, ZrO$_2$, Ta$_2$O$_5$, and (Ba, Sr) TiO$_3$, have been studied for the application in storage capacitors of next generation dynamic random access memory (DRAM). Ruthenium is one of the promising electrode materials which are compatible with these high-k dielectrics. Ruthenium exhibits characteristics of high work function, good etching property with oxygen plasma and low resistivity. For these reasons, ruthenium thin film has been extensively studied for the next candidate material as an electrode for capacitors of DRAM. However, the Ru deposition shows long incubation time before actual deposition. Thus, the detail investigation of this incubation time and correlation with initial growth mechanism is very important to monitor the growth mechanism. To study the growth mechanism of Ru, we prepared several different SiO$_2$ substrates grown under different conditions by CVD method, thermally grown, and grown in wet atmosphere. Ruthenium films were deposited on these various SiO$_2$ substrates by remote plasma ALD method. We used bis(ethyl-π-cyclopentadienyl) ruthenium [Ru(EtCp)$_2$, Ru(C$_2$H$_5$C$_5$H$_4$)$_2$] as a ruthenium precursor and NH$_3$ plasma as a reactant. In this experiment, the remote plasma atomic layer deposition (RPALD) method with NH$_3$ plasma is used to deposit ruthenium thin films. The characteristics and initial growth of Ru on the different SiO$_2$ substrates were measured with many analysis tools. The characteristic of differently grown SiO$_2$ was investigated by X-ray reflectivity (XRR). And the surface morphologies of ruthenium films were examined by field emission scanning electron microscope (FESEM) and atomic force microscope (AFM). We also analyzed chemical states of the ruthenium films with X-ray photoelectron spectroscopy (XPS). The chemical composition and impurity content were investigated by Auger electron spectroscopy (AES). The phase identifications of the samples were performed by X-ray diffraction (XRD).

TF-ThP36 Electrical Characteristics of Lanthanum Oxide with SiO$_2$ Buffer Layer using Remote Plasma Atomic Layer Deposition (RPALD) Method, ***H.R. Lee**, S.H. Woo, H.C. Kim, J.S. Lee, H.G. Kim, Y.C. Kim, H.T. Jeon*, Hanyang University, Republic of Korea

Conventional SiO$_2$ has been used as a gate dielectric in complementary metal oxide semiconductor (CMOS) devices. When high-k materials are used as new gate oxides instead of SiO$_2$, the film thickness can be increased to reduce the tunneling leakage current while scaling the equivalent oxide thickness (EOT). Atomic layer deposition (ALD) method has been studied in an effort to deposit high-k materials. Especially, the plasma- enhanced atomic layer deposition (PEALD) method is applied for deposition of high-k dielectrics due to its advantages such as an increased reactivity, reduced impurities, and a good uniformity. Lanthanum oxide (La$_2$O$_3$) is considered as one of the most promising materials among these high-k materials for the following reasons. It has high dielectric constant (k=20-30), large band gap, and good thermal stability on Si substrate. However, one of the difficulties in the application of the La$_2$O$_3$ to MOSFETs is a large flat-band voltage shift. The undesirable large flat-band voltage shift results from two kinds of defects. One is a fixed oxide charge located at the interface between the oxide and Si, and the other is an oxide trap charge in the oxide. Lanthanum silicate interlayer,which is formed between La$_2$O$_3$ and silicon substrate, has defects that can shift flat-band voltage. Therefore, it is desirable to reduce impact of these defects for the application of lanthanum oxide.

In this study, a SiO_2 buffer layer was used to improve the electrical properties of La_2O_3 gate oxides. The SiO_2 buffer layer retards the formation of lanthanum silicate interlayer, thus reducing the fixed oxide charges. We have examined the La_2O_3 films which were deposited on Si substrate and thermally grown SiO_2 buffer layer using PEALD method, respectively. La_2O_3 growth rate was 0.3 nm/cycle at 300 ºC on Si substrate and flat-band voltage was 0.29 V. Leakage current was 5.67E-8 A/cm^2 at . We analyzed a composition and chemical bonding of the films with X-ray photoelectron spectroscopy (XPS). Electrical characteristics were also measured using an Agilent B1500A semiconductor parameter analyzer to investigate the flat-band voltage and the equivalent oxide thickness (EOT).

TF-ThP37 Chemical Vapor Deposition of Samarium Doped Ceria from Metal-Organic Solid Precursors

T.-S. Oh*, D. Boyd, S. Haile*, Caltech

Doped ceria (where the dopant is a trivalent cation such as Sm or Gd) is an attractive electrolyte material for solid oxide fuel cells (SOFCs) owing to its high ionic conductivity at intermediate temperatures (IT). It is also a good anode material due to its mixed ionic-electronic conduction under the reducing conditions that exist at a fuel cell anode. For high power density, the electrolyte in a fuel cell must be fabricated in thin film form in order to lower the area specific resistance. Accordingly, many studies have been directed towards thin-film preparation of the conventional SOFC electrolyte material, yttria stabilized zirconia. In the present work, samarium doped ceria (SDC) thin films are grown via metal-organic chemical vapor deposition (MOCVD) as a first step towards high power density SDC based fuel cells.

A vertical cold-wall MOCVD reactor was built in-house. This cold-wall reactor has a showerhead which gives impinging multi-jet flow of precursor vapor onto a substrate of choice. Metal organic precursors, $Ce(tmhd)_4$ for Ce and $Sm(tmhd)_3$ for Sm, were utilized as the cation source compounds. They are commercially available as fine powders. These were used in the form of fine solid powder coated on steel balls by mechanical stirring. This step is expected to provide uniform mixing of the two precursors with sufficient, stable surface area for evaporation. During a deposition run, minimum surface area change for the solid precursors is desired. The compound mixture was placed in a single evaporation vessel for the simplicity of the system, and the evaporation temperature was controlled.

Precise and reproducible control of composition is not trivial for solid solutions such as samarium doped ceria. An UV optical cell is located between the precursor evaporator and the deposition chamber. Optical absorption of the incoming precursor vapors was monitored in-situ. Even though it is impossible to separate peaks from the two metal-organics due to severe peak overlap, gas phase UV absorption still provide valuable information on evaporation behavior. In-line gas phase reaction forms oxide powders before precursors reach the substrate, and therefore should be suppressed. UV absorption can detect this unwanted reaction. The influence of deposition conditions such as substrate temperature, evaporation temperature, and precursor mixing ratio, on the the samarium content in the oxide thin films is explored. Deposition is carried out on single crystalline oxide wafers, and nickel-SDC cermet pellets. The resulting films were characterized by scanning electron microscopy (SEM), Raman spectroscopy, X-ray diffraction and energy dispersive X-ray spectroscopy (EDS).

TF-ThP38 Characterization of OTFT Fabricated Using Ink Jet Combined with Imprint Technology

K.H. Kim*, K.H. Eum, I.S. Chung*, Sungkyunkwan University, Korea

We fabricated organic thin film transistor using ink jet printing combined with a nano imprint. The channel length of OTFT were in the range between 2 um and 7 um. TIPS pentacene was used as an active material to achieve the better mobility. Additionally, Poly-4-vinylphenol (PVP) was chosen as a gate insulator. All materials including Ag electrode were prepared using ink jet printer (UJ-200) on polyethersulphone (PES) substrate. The physical properties were analyzed using SPM and SEM. The electrical characterization was done using Keithley-4200.

TF-ThP39 Fabrication and Characterization of Ink Jet Processed Organic Thin Film Transistors with Poly-4-Vinylphenol (PVP) Dielectric

K.H. Eum*, K.H. Kim, Y.K. Son, I.S. Chung*, Sungkyunkwan University, Korea

We fabricated organic thin film transistors (OTFTs) with a 6,13-bis(triisopropylsilylethynyl) (TIPS) pentacene as an active layer and cross-linked poly-4-vinylphenol (PVP) as a gate dielectric using ink-jet print. We used polyethersulphone (PES) as a substrate and Au as foe electrode. Prior to adopt PVP as a gate dielectric, PVP print condition was derived from metal-insulator-metal (MIM) structure by comparing with spin coating process in terms of leakage current, breakdown voltage and dielectric constant. The electrical properties were obtained using Keithley 4200 unit and Boonton 7200 capacitance meter. Additionally, the physical properties were also obtained using scanning probe microscopy SPM and scanning electron microscope (SEM).

TF-ThP40 Improvement of Ohmic Contact Property of a Inkjet Printed TIPS-pentacene Schottky Diode by Employing SAM and PEDOT:PSS Layers

J.M. Kwon*, K.H. Kim, J.H. Heo, I.S. Chung*, Sungkyunkwan University, Korea

Inkjet printing technology has attracted a large of attention increasingly because of its low cost fabrication, capability with flexible substrate and high-throughput. Especially, organic schottky diode is thought to play an important role to operate a Radio Frequency Identification (RFID) at high frequency. In this paper, we fabricated organic schottky diodes using inkjet printer with two different sizes of diameters, namely, 50um and 30um. Au was deposited on polyethersulfone (PES) substrate, and then printed 6,13-bis(tri-isopropylsilylethynyl) pentacene (TIPS - pentacene) using ink-jet printer. Finally, Silver was form schottky contact with TIPS-pentacene layer. In an effort to improve ohmic contact, we utilized self-assembled-monolayer (SAM) and Poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate) (PEDOT:PSS) between gold and TIPS- pentacene layer, respectively. Keithley 4200 and Scanning probe microscopy (SPM) were used to examine the physical and electrical properties.

TF-ThP41 Solution-derived Nanocomposite Materials for Photovolytaics

E. Ryabova, NViA, *M. Shkolnikov*, ADCO-Engineering

Photovoltaics are in a verge of expansion challenged with the grid parity requirement.

Three generations of solar cell technologies are racing for the better $$/Wp numbers.

c-Si, mc-Si, micromorph, Thin film (CdTe, CIGS), Organic – all use thin film processing in order to create absorber, emitter, light trap-assisting layer, back side field -passivating layer, barriers, metallization, etc.

In order to achieve grid parity ($$/Wp) PV-technology strives to increase Power Conversion Efficiency (PCE) coupled with reduced Cost of Ownership (CoO).

Former is done by minimizing losses -optical and electrical and implies advanced interface engineering.

Later entails low cost material and technology utilization that places verdict on industry trend toward innovative technologies.

Wet chemistry based thin film deposition routing is proposed to replace high vacuum ones for several critical layers, such as ARC, TCO, BSF and surface modification.

This low cost method features:

High deposition rate

High material utilization

Simple equipment capable of very large substrate handling.

Ideal for roll-to-roll operation

Full conformity with complex shape surfaces

Highly uniform films of various compositions with the thickness range 6-600 nm have been deposited using dip coating, slot die and microgravure coating, spray coating.

With the proper surface activation film forms covalent bonds with the substrate and has no interfacial imperfectness.

When used for solar cell fabrication – can add up to couple of percent to PCE compare to traditionally processed cells.

Precursor for the specific layer can be purchased or mixed in-house depends on formulation.

Solution Derived Nanocomposites are already on their way to mass production at many PV-houses with the increasing popularity among large size, flexible substrate, and concentrating solar users.

TF-ThP42 Experimental Evaluation of Cheap, Overly Abundant Semiconductor Materials for Wide-Spread Photovoltaic Applications

K. Davis*, S. Nason, N. Hickman*, Florida Solar Energy Center

Only a limited amount of semiconductor materials have been deployed on a wide-spread basis for terrestrial solar energy production. Single crystalline silicon has held the majority of the market share, with other technologies emerging over the years with a smaller presence (e.g. a-Si:H, CdTe, CIGS). Some of the materials used in many of these technologies possess clear long-term disadvantages with regards to economics, availability, and environmental consequences. A recent study of 23 potential semiconductors ranks the potential of each in regards to their annual electricity production potential and their raw material cost [1]. Detailed experimental research on the photovoltaic potential of many of these individual compounds is very sparse or non-existent.

In this experimental study, seven of the best candidates were selected for further investigation, including FeS_2, Zn_3P_2, PbS, CuO, CuO_2, NiS, and ZnSe. Transmission, reflection, and absorption measurements were performed on these binary compounds. Solar cells were also fabricated at the Florida Solar Energy Center to measure photovoltaic properties, including conversion efficiency under Standard Test Conditions, quantum efficiency and spectral response. The measured optical and electrical properties of these semiconductor materials provides a better understanding of the potential of each for wide-spread deployment. Future work will be focused toward optimizing device design and fabrication processes to maximize the energy conversion of the best potential compounds.

1. C. Wadia, A.P. Alivisatos, D.K. Kammen, Environmental Science and Technology, 2009, 43 (6), 2072-2077

TF-ThP43 Investigation of Microstructure, Surface Morphology, and Hardness Properties of PtIr Films by Magnetron Sputtering, ***C.-T. Lee***, *B.H. Liou, C.-M. Chang, Y.W. Lin*, Instrument Technology Research Center, National Applied Research Laboratories, Taiwan

$Pt_{1-x}Ir_x$ films with x = 22.76-63.25 are fabricated on (100) Si substrates at 400 ℃ by magnetron sputtering deposition. Effects of Ir content on the microstructure, morphology and hardness of PtIr films are investigated by field emission scanning electron microscopy, X-ray diffraction, atomic force microscopy and nanoindentation system. The columnar structures are observed by field emission scanning electron microscopy. X-ray diffraction analysis revealed that PtIr films had preferred orientation along Pt(111) as Ir content is below 50.84 at.%. When the Ir content is more than 50.84 at.%, the PtIr film had another preferred orientation, Ir(111).The surface morphology is analyzed by atomic force microscopy. Roughness of PtIr films is decreased with increased Ir content. The hardness of all PtIr films is under 20 GPa. It is found the maximum hardness of PtIr films is about 14.9 GPa as Ir content is 57.9 at.%.

TF-ThP44 Effect of Hydrogen Plasma Pretreatment on Superconformal Cu Gap-Filling of Trench with Ru Barrier Metal, ***H.K. Moon***, *S. Kim, C.R. Jung,* SungKyunkwan University, South Korea*, W. Kim, H. Kim,* Pohang University of Science and Technology, Korea*, N.-E. Lee*, SungKyunkwan University, South Korea

In this work, effects of hydrogen plasma pretreatment on superconformal Cu gap-filling of the nano-scale trench with atomic-layer –deposited (ALD) Ru barrier metal were investigated. For this purpose, hydrogen plasma pretreatments on ALD-Ru layer were carried to control the nucleation and growth of Cu during metal-organic chemical vapor deposition (MOCVD). As the plasma pretreatment time increases, Cu nucleation is suppressed increasingly. XPS and thermal desorption experiments of the pretreated ALD Ru surface showed that hydrogen atoms passivate the Ru surface, which leads to suppression of Cu nucleation presumably due to inhibition of adsorption of Cu MO precursors. During Cu gap-filling of the sub 60-nm and ALD-Ru deposited trenches without the plasma pretreatment, the entrance of the trenches during copper deposition was were easily blocked. On the contrary, for the plasma pretreated trenches, evolution of Cu layer in the trenches showed a dramatic reduction of over-hang near the entrance of the trench leading to superconformal filling of the nano-scale trench.

Tribology Focus Topic
Room: Hall 3 - Session TR-ThP

Tribology Poster Session

TR-ThP1 XPS Study of Ti Surface Reactivity under Friction in Various Nitrogen Environments, ***T. Le-Mogne***, *C. Mary, J.M. Martin*, Ecole Centrale de Lyon, France

Thanks to their high strength to weight ratio and good corrosion resistance, Ti alloys are widely used for various industrial applications and may be exposed to several environmental conditions. In a previous study, the authors have pointed out the evidence of titanium tribochemical reaction with nitrogen under fretting in air.

In order to investigate this phenomenon and especially the effect of friction on the nitriding mechanisms of Ti alloys, an experimental simulation was conducted in a specific Environment-Controlled Tribometer (ECT) coupled with in-situ X-ray Photo-electron Spectroscopy (XPS) analysis. Several Ti/Ti reciprocating sliding tests were performed with a pin on flat geometry successively in high vacuum, in N_2 environment and in air. The objectives were to investigate the reactivity of Ti surfaces with nitrogen in several tribological situations: after removal of native oxide layer by Ar+ etching, after friction under vacuum followed by N_2 exposure and after friction under N_2 environment. This approach proposes conditions needed for Titanium reaction with nitrogen.

TR-ThP2 Friction and Sliding Wear Behavior of nc-TiN/a-Si_3N_4 Nanostructured Coatings, ***J. Garcia***, *M. Flores*, Universidad de Guadalajara, Mexico

The present work is related to the evaluation of dry sliding wear resistance of a sputtered PVD nanostructured nc-TiN/a-Si_3N_4 coating, deposited on Stainless steel 316L substrates. X-ray diffraction is used to analyze the nanostructure of the film. The topography of substrates, films and Wore Surfaces were analyzed by profilometry. Film adhesion to the substrate was evaluated by scratch-tests. The surface hardness was measured with a Vickers micro-hardness tester. The wear resistance was evaluated by Pin-on disk under a normal load in the range of 2 to 10 N and a constant tangential speed of 0.15 m/s and reciprocating apparatus with a frequency of 1 Hz and a normal load within the same range established above, both tests in dry conditions. After these tests, on the coating as well as on the counterpart, the wear mechanisms developed were analyzed by Optical Microscopy, the wear tracks were measured and the wear rate was calculated and discussed.

Friday Morning, November 13, 2009

Applied Surface Science
Room: C2 - Session AS-FrM

Practical Surface Analysis
Moderator: S.R. Bryan, Physical Electronics

8:20am **AS-FrM1 Combined XPS and AES Characterization of Nano Structures Developed for Advanced Energy Conversion and Storage Materials**, ***C. Hitzman***, Stanford University **INVITED**

Ultra-Thin films, Nano-Particles and Nano-Wires are at the center of research for new materials for use in Photonics, Nano-Electronics and Advanced Energy Conversion and Storage. Metals, Semiconductors, Glasses and Polymers are all being investigated for these applications. Understanding the structure, composition and chemistry of these new materials is essential in advancing their development.

X-ray Photoelectron Spectroscopy (XPS) is one of the most commonly used surface techniques for quantitative measurements of elemental composition and specific chemical information of surface constituents. Angle Resolved XPS and XPS combined with ion sputtering can provide information beyond the surface of the material. There are some limitations, however, in the special resolution of XPS.

Auger Electron Spectroscopy (AES) can provided elemental information with high spatial resolution. This is extremely useful in obtaining localized information from Nano Particles and Nano Wires.

The combination of the XPS and AES techniques can further advance the development of these new material. In this presentation we will look at complimenting and correlating data obtained by XPS and AES from a variety of advanced materials from a host of application areas.

9:00am **AS-FrM3 Investigation of Internal Structure of Drug Products by TOF-SIMS and CT**, ***X. Dong***, *C.A.J. Kemp*, Eli Lilly and Company

The properties of API and excipients can influence the manufacturing process and the quality attributes of the dosage form. It is known that particle size, shape, and agglomeration of the drug substance and excipients affect flow properties, dissolution behavior, dose uniformity and bioavailability of the formulation. Therefore, there is a key interest in pharmaceutical development to understand how the ingredients of the formulation are blended in the various stages of the production process, as well as how various components distribute in solid dosage form. TOF-SIMS has been applied to provide chemical images for various drug products. Due to the surface sensitivity of this technique, the images could be affected by potential smearing during sample preparation. To better understand the effect of sample preparation, TOF-SIMS images obtained from drug products are compared with micro-CT images, which are obtained non-destructively. In addition, the effects of C_{60} sputtering on drug molecule and excipeints, as well as on TOF-SIMS images are also investigated.

9:20am **AS-FrM4 Effectiveness of Passivation Techniques on Hydrogen Desorption in a Pure Tritium Environment**, ***S. Woodall***, *E. Pines, D. Valles-Rosales*, New Mexico State University

This research compared protium outgrowth of different passivation surfaces in a low pressure environment. Tritium is a radioactive isotope of hydrogen. It is used as a fuel in fusion reactors, a booster material in nuclear weapons and as a light source in commercial applications. When used in fusion reactors, and especially when used in the manufacture of nuclear weapons, purity is critical. For Department of Energy use, tritium is routinely recycled by Savannah River Site and is produced and stored at 99.99% purity. For use elsewhere in the country, it must be shipped and stored, while maintaining the highest purity possible. As an isotope of hydrogen it exchanges easily with the most common isotope of hydrogen, protium. Stainless steel bottles are used to transport and store tritium. Protium, present in air, becomes associated in and on the surface of stainless steel during and after the manufacture of the steel. Therefore, the stainless steel bottles contribute to the contamination of the tritium with protium. This research is to determine how effective different passivation techniques are in minimizing the contamination of tritium with protium. Additionally, this research will attempt to determine a relationship between surface chemistry of passivated steels and protium contamination of tritium.

9:40am **AS-FrM5 Comparison of Supported Catalyst Particle Size Determination by Low Energy Ion Scattering (LEIS) and Transmission Electron Microscopy (TEM)**, *R.A.P. Smith, D. Ozkaya,* Johnson Matthey Technology Centre, UK, *H. Brongersma,* ***T. Grehl***, ION-TOF GmbH, Germany, *H.R.J. ter Veen*, Tascon GmbH, Germany

Particle size determination for supported metal catalysts is vital for the technological improvement of such systems in most areas of catalysis; automotive emission control catalysts, fuel cell materials to name but two. Improved measurements of the dispersion of a supported metal can be fed into product research and development with benefits including improved control of metal deposition and thereby, ultimately, efficient material use, particularly when the supported metal is from the platinum group of metals and so very expensive. The particle sizes of interest for many supported metal catalysts are in a single-digit nanometre range and for many techniques this poses a problem.

TEM is one of a limited number of techniques that can be applied in this particle size range but there is an inherent statistical difficulty - the areas studied are limited so might not be truly representative of a well-dispersed material although any information obtained is usually very accurate.

As a laboratory technique rather than large-scale facility such as is often required for effective spectroscopic determination of particle size, LEIS is of great potential use in this area. LEIS signals are directly related to the surface area of a given element that is exposed for the study and a reduction in particle size leads to higher surface area to volume ratio and therefore inherently larger signal from scattered ions for the amount of material present. In addition, although the single outermost layer of a surface is the principal signal of interest, a signal due to ions scattered from deeper layers can be measured and is useful for determination of extremely thin (up to 10 nm) layers. This makes the technique useful for electronics applications but it can also be applied to characterise how "thick" a particle is, leading to a second method of particle size determination. For these two reasons, smaller particles yield good information when studied by LEIS. The technique is a large-area (1 mm scale) technique so provides statistically representative average information. LEIS also has advantages over TEM in that it works just as easily on supports with heavy elements (zirconia, ceria) as light elements (carbon, alumina).

In this presentation we show results of a comparative study of LEIS and TEM used for the characterisation of model fuel cell materials, specifically platinum supported on carbon with a range of particle sizes under 10 nanometres. The results show that LEIS is an effective laboratory technique that can provide excellent characterisation data on small particles that can be correlated with other techniques to improve understanding of commercial systems.

10:00am **AS-FrM6 Characterization of Organic Light Emitting Devices Via Surface Analysis and Electron Microscopy**, ***D.J. Gaspar***, *A.S. Lea, A.B. Padmaperuma, Z. Zhu, D.W. Matson, L. Wang,* Pacific Northwest National Laboratory, *J. Berry, D.S. Ginley*, National Renewable Energy Laboratory

The development of energy efficient organic light emitting devices (OLEDs) for solid state white lighting is a goal of the US Department of Energy. Key challenges facing the development of these materials include materials stability and device lifetime, particularly for blue phosphorescent devices, a necessary component of a white OLED device. Due to the high exciton energy necessary to generate blue light (i.e., quenching and side reactions more easily occur), the stability and lifetime of these devices is a particular challenge. There are many mechanisms by which a device may fail, including interfacial and bulk reactions, diffusion of components within or between layers, and structural and/or phase changes within one or more components. A great deal of work has been done to elucidate mechanisms of degradation, including through chemical and physical failure analysis of components and devices. We present here some of our work to elucidate chemical and physical changes in OLEDs devices and components using surface analysis and electron microscopy. We have used various tools including X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectrometry (TOF-SIMS), focused ion beam (FIB) combined with both electron microscopy (scanning and transmission), X-ray diffraction and atomic force microscopy (AFM, including conductive AFM). This talk will focus on characterization of devices incorporating new materials including transparent conducting oxides, host, and electron- and hole-transporting materials.

10:20am **AS-FrM7 Structure and Composition of Plasma Treated Polystyrene Surfaces Determined by Complementary Analytical Techniques**, ***P. Mack**, R.G. White, T. Carney,* Thermo Fisher Scientific, UK, *E.H. Lock, S.G. Walton,* Naval Research Laboratory, *D.Y. Petrovykh*, Naval Research Laboratory and University of Maryland

Plasma-treatment of polymers produces materials that exhibit a wide range of surface compositions, properties, and structures. A new low-energy plasma treatment method aims to modify only the top few nanometres of polymer films, producing surfaces that pose challenges and offer opportunities for quantitative surface analysis. Using a variety of complementary analytical techniques maximizes the information available to the analyst.

High-quality polystyrene films were spin-coated onto silicon substrates and treated with low-energy plasmas generated by electron beams in different environments, including oxygen, nitrogen, and SF6. Atomic Force Microscopy was used to determine surface roughness and contact angle measurements were used to determine the hydrophobicity of the plasma-modified surfaces. The Thermo Scientific Theta Probe, an XPS system that provides a unique parallel-detection capability for angle-resolved XPS (PARXPS) and REELS measurements, was used to investigate the chemical and structural transformations produced by different plasmas.

The chemical changes produced by plasma treatments were examined by high energy resolution XPS, and PARXPS data were analyzed using maximum-entropy calculations to obtain non-destructive depth profiles of these chemical changes. Complementary REELS measurements were used to examine the level of carbon unsaturation at the uppermost surface of each of the plasma modified polystyrene films. The non-destructive PARXPS depth profiles were also compared with high-resolution low-energy ion sputter profiles measured in a Thermo Scientific K-Alpha system. The depth profiles obtained using several surface analysis methods confirmed that the chemical changes produced by the low-energy plasma modification are confined to the top 2–3 nm of the polymer surfaces. The observed depth distribution of unsaturated carbon species is also consistent with polystyrene surfaces undergoing "hydrophobic recovery" after treatments in oxygen and nitrogen plasmas.

This work was supported by the Office of Naval Research.

E. H. Lock is NRL/NRC Postdoctoral Research Associate.

10:40am **AS-FrM8 An Investigation of Detection Limits and Common Interference Factors in Depth Profiling Hydrogen and Deuterium by Time-of-Flight Secondary Ion Mass Spectrometry**, ***Z. Zhu**, V. Shutthanandan*, Pacific Northwest National Laboratory

Hydrogen depth distribution is very important information in today's novel material research. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been used for this task for quite a while. Normally, dual beam strategy, in which a cesium ion beam is used for sputtering, and a primary ion beam (Ga^+, In^+, Au^+, Bi^+ …) is used for measurement, is applied in hydrogen depth profiling. Residual gas in vacuum chamber has been found to significantly interference SIMS hydrogen depth profiling, so that deuterium is introduced to substitute hydrogen for SIMS analysis if feasible. Apparently, the information of detection limits and common interference factors are very important for ToF-SIMS users, but such information was not easily available. In this work, we investigated detection limits of hydrogen and deuterium in four widely used materials, including silicon wafer, quartz, zinc oxide and titanium oxide. Deuterium ions were quantitatively implanted into these samples, and they were used as the standard to evaluate detection limits of both hydrogen and deuterium. It is found that hydrogen detection limit is about 100-400ppm, limited by residue gas interference. On the other hand, detection limit of deuterium can be as low as 1-10ppm due to no interference. These results will be discussed along with some common interference factors.

11:00am **AS-FrM9 Ultra-Low-Angle-Microtomy to Prepare Fuel Cell Membrane Electrode Assemblies for XPS Analysis**, *K.S. Reeves, K.L. More,* Oak Ridge National Laboratory, *R.G. White, T.S. Nunney, A.E. Wright,* Thermo Fisher Scientific, UK, ***H.M. Meyer III***, Oak Ridge National Laboratory

Membrane electrode assemblies (MEA) were examined before and after use in a hydrogen fuel cell. MEAs consisted of anode and cathode (both comprised of carbon and Pt-catalyst) separated by a polymeric proton exchange membrane (PEM) made from Nafion®. Of particular interest is through-depth compositional uniformity of the membranes after use. PEMs are typically 20-50 microns thick and as such, the use of surface sensitive techniques to probe their through-depth composition requires unique sample preparation. Traditional Ar-ion depth profiling is not possible since even low energy (200-500 eV) Ar ions disrupt the polymer structure and chemical bonding. Polyatomic sputter systems developed for etching polymer surfaces without imparting damage are also of little use due to low sputter rates (~0.1 nm/s). Even with a carefully prepared cross-section of the MEA (routinely done for TEM sample prep), only limited information is obtained using the relatively large x-ray spots (10's-to-100's of microns) of most XPS instruments. To probe the inner region of the membrane film, we have developed an ultra-low-angle microtomy (ULAM) sample preparation technique. The ULAM technique is similar to metallographic low-angle lapping and is based on similar methods described by Watts and co-workers [1]. The ULAM-derived taper through a ~25 micron thick membrane effectively extends the cross-section to greater than 400 microns. With this exaggerated cross-section, the 30 micron X-ray spot of our Thermo Fisher Scientific K-Alpha XPS instrument was able to evaluate composition as a function of depth from the anode, across the membrane to the cathode. Core level and VB spectra from the anode, cathode, and membrane components will be presented for a fresh MEA and for the same MEA after 500 hrs of use. To demonstrate the effectiveness of the ULAM technique, data from samples prepared using ULAM will be compared to surfaces of free-standing membrane films and from standard cross-sections.

Research supported by the U.S. Dept. of Energy, Office of Energy Efficiency and Renewable Energy, Hydrogen, Fuel Cell, and Infrastructure Technologies Program. Research at the ORNL SHaRE User Facility was sponsored by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Dept. of Energy.

[1] S.J. Hinder, C. Lowe, J.T. Maxted, J.F.Watts, Journal of Materials Science **40** (2005) 285-293.

11:20am **AS-FrM10 Acquisition of Quantitative Implant Coverage Maps of Semiconductor Devices with ToF-SIMS**, ***J.A. Ohlhausen**, M.L. Anderson, J.J. Sniegowski*, Sandia National Laboratories

Secondary Ion Mass Spectrometry (SIMS) is commonly used to acquire quantitative implant profiles in Si-based semiconductors. While dynamic SIMS is the preferred technique due to its sensitivity, Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) can also be used. The benefit of ToF-SIMS is that the full spectrum is acquired instead of a few selected species. Thus, unexpected species can be retrospectively included in the analysis in post-processing. Typically when measuring implant profiles, SIMS is used to verify a dose and depth distribution as quality control on single wafers from a single fab implant tool. Data from large areas are required to ensure that signal-to-noise levels are reasonable. Occasionally, it is important to measure implant doses on completed or near-completed devices. When this is the case, one no longer has large uniform areas from which to acquire high signal-to-noise data. Instead, the actual implant information is spatially patterned and may be vertically distinct, therefore containing multiple vertical layers. 3D measurements can be performed to determine the spatial distribution of major device constituents, such as metallization lines and insulating paths, but it is very difficult to determine quantitative implant information while measuring the full 3D distribution. This difficulty arises from the inherently low signal-to-noise measurement that cannot be helped by the use of spatial binning. To some extent, these issues can be overcome in ToF-SIMS as the user has independent control over sputter rate and acquisition times. Methods for preparing samples and acquiring data have been developed along with processing protocols to quantify the implant coverage and 3D distribution of implants in semiconductor devices using ToF-SIMS. These procedures, examples and limitations of the technique will be discussed.

†Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:40am **AS-FrM11 Investigations of Interactions Between Hafnium and Carbon During High Temperature Anneals**, ***B.R. Rogers**, R.D. Geil, B.W. Schmidt*, Vanderbilt University

Results from studies investigating inter-diffusion and reactions occurring between sputtered hafnium layers and carbon substrates will be presented. Hafnium carbide is a ultra-high temperature material of interest to the aerospace and other communities. Our investigations provide fundamental properties such as diffusivities and reaction activation energies needed for materials design. Samples are annealed in inert and vacuum environments and then are characterized using XPS, ion-beam backscattering, AES, and XRD to pull out the parameters of interest.

Biomaterial Interfaces
Room: K - Session BI+AS+NS-FrM

Micro and Nanoengineering of Biointerfaces II
Moderator: E.O. Reimhult, ETH Zurich, Switzerland

8:20am **BI+AS+NS-FrM1 Colloid Crystal Surface Patterning for Studying Biointerface Phenomena**, ***P. Kingshott***, Aarhus University, Denmark **INVITED**

Patterning of many types of biomolecules over length scales ranging from micrometers to nanometers is of great interest for biosensors, cell culture dishes, medical implants and tissue engineering. Ideally these devices 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 and electron beam 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 colloid patterns, with controllable dimensions, can be generated from simple self-assembly of large and small particles onto surfaces, where single layers of large particles are surrounded by crystals of smaller particles. In addition, when the particles are pre-coated with proteins (e.g. albumin, lysozyme and antibodies) the assembly process also takes place. This opens up the possibility of patterning many proteins on one substrate with controllable dimensions and high order. The crystals are also used to generate chemical patterns since the large particles act as a mask during, for example sputtering of Au, since the region in contact with the substrate remains uncoated. The thickness of gold features can be controlled by the sputtering time. 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, such as FITC-labelled antibodies or rhodamine-labelled albumin, only onto the Si regions of the pattern. In another approach, binary patterns made from silica and amine polystyrene particles are heated at 100 ºC (above glass transition temperature of polystyrene) followed by etching with HF to remove the silica particles creating highly ordered 2- and 3D porous substrates. In summary, we introduce a novel method for generating highly-ordered patterns from colloid crystals that is very fast, inexpensive, and allows patterns of multiple biomolecules over large areas in 2- and 3D.

9:00am **BI+AS+NS-FrM3 Biological Nanoarrays: from Protein-DNA Interaction Studies to Cell Adhesion Investigations**, ***M. Palma***, *J. Abramson, M. Schvartzmann, A. Gorodetsky, C. Nuckolls, M.P. Sheetz, J. Hone, S.J. Wind*, Columbia University

Nanopatterned arrays of biomolecules are a powerful tool to address fundamental issues in many areas of biology.

Combining nanolithography and biomolecular self-assembly strategies, we report on the fabrication of nanopatterned biomimetic surfaces and their use in a variety of biological studies.

We have fabricated arrays of Au/Pd nano-dots of dimensions down to the sub-10nm regime using electron-beam and nanoimprint lithography. Different chemical strategies at surfaces have been pursued to organize biological relevant nanoarchitectures into hierarchical arrays in which structural parameters, such as the spacing and nature of specific functional groups, could be systematically varied and controlled.

The generation of DNA nano-dot arrays allowed us to follow the activity (at surfaces) of a restriction enzyme in real time and at the nanoscale: fluorescence microscopy enabled the monitoring of the kinetics of such protein-DNA interaction.

Furthermore we will show how our nanopatterned biomimetic surfaces can be used to probe the importance of both the geometric arrangement (i.e. spatial ordering of transmembrane proteins, integrins) as well as the role played by peptide sequences as cell binding domains in the formation of cell focal adhesions.

Finally, we will highlight the broader utility and application of such functional nanopatterned surfaces for nanoscopic control and studies: biochemical specificity can be used to selectively place individual nanocomponents with a high degree of control over both position and orientation, as well as to organize functional nanostructures into dense arrays with very fine pitch.

9:20am **BI+AS+NS-FrM4 Arbitrary Topographical Patterns Fabrication by using Two-Photon Photopolymerization**, ***H.J. Jeon***, University of California, Berkeley, *H. Hidai,* Tokyo Institute of Technology, Japan, *D.J. Hwang, K.E. Healy, C.P. Grigoropoulos*, University of California, Berkeley

Two photon photopolymerization (TPP) is a direct laser writing technique, which is known as a powerful tool to make arbitrary 3D structures. Here we demonstrate a method for fabricating high aspect ratio (~10) patterns of varying height by using TPP process in order to study contact guidance of cells. Ridge patterns of various heights and widths were fabricated through single laser scanning steps by low numerical aperture optics, hence at much higher processing throughput. Fibroblast cells were seeded on parallel line patterns of different height (~1.5-µm, ~0.8-µm, and ~0.5-µm) and orthogonal mesh patterns (~8-µm and ~4-µm height, ~5-µm and ~5.5-µm height, and ~5-µm and ~6-µm height). Cells experienced different strength of contact guidance depending on the ridge height. Furthermore, cell morphology and motility on microscale anisotropic cross patterns and parallel line patterns in different aspect ratio (1:2, 1:4, and 1:∞), size of grid (12-, 16-, and 24-µm distance neighboring longer side ridges) was also studied quantitatively. The significant effect of the cross patterns on cell alignment and directionality of migration, and motility was observed on 1:4 cross patterns and parallel line patterns, even though all cross patterns could have an effect on cell attachment and morphology. Overall, it is noted that cell morphology and motility can be influenced by the height of ridges, the aspect ratio of cross pattern and the size of grid.

9:40am **BI+AS+NS-FrM5 2D & 3D Nanoarrayed Chemical Contrasts for Better Biorecognition Kinetics**, ***G.R. Marchesini***, *P. Lisboa, A. Valsesia, C. Pascual, P. Colpo, F. Rossi*, Joint Research Centre, European Commission, Italy

Monitoring biomolecular recognition events with Surface Plasmon Resonance (SPR) heavily relies on the right surface chemistry. Uniform self assembled monolayers with carboxylic functional groups are widely used but might show steric hindrance, thus limiting the interpretation of the biorecognition kinetics. Furthermore, such negatively charged surface needs to be passivated upon immobilization of the ligand to prevent nonspecific electrostatic-driven binding of components from the analyte matrix.

In the present study we evaluate alternatives based on a 2D and 3D array of carboxylic nanodomains on a chemically contrasting matrix. By means of plasma-based colloidal lithography and e-beam lithography we were able to array ≈ 200 nm wide carboxylic motifs having a hexagonal 2-D crystalline structure on a gold surface. The interstitial gold was further modified with contrasting thiol chemistries or vapour enhanced deposition of nonadhesive material like poly ethylene oxide (PEO). The two 2D nanoarrayed chemical contrasts evaluated were carboxylic nanodomains on either a methyl-based or PEO-based matrix.

In addition, the 3D nanoarray based on a carboxylated dextran hydrogel matrix was evaluated for effects on the mass transport. In these cases, mass transport is one of the major challenges when measuring binding kinetics of biointeractants on a surface using a surface plasmon resonance (SPR) biosensor. The presence of a hydrogel on the surface increases the interactant density improving the sensitivity. Nevertheless, this is done at the expense of aggravating the mass transport phenomena.

The influence of the nanoarrayed chemical contrasts combined with the sensitivity improvement due to the band-gap effect on the kinetics of model biomolecular interactants was evaluated using an imaging SPR system and correlated with surface characterization techniques as atomic force microscopy, ellipsometry, and contact angle measurements.

10:00am **BI+AS+NS-FrM6 Spatially Selective Deposition of a Zwitterion with Alkyl Pendant Groups on Periodically Poled Lithium Niobate**, ***Z.Z. Zhang***, *J. Xiao,* University of Nebraska-Lincoln, *D. Wu,* North Carolina State University, *A. Gruverman,* University of Nebraska-Lincoln, *L. Routaboul, P. Braunstein, B. Doudin,* Université Louis Pasteur Strasbourg, France, *O. Kizilkaya,* Louisiana State University, *C. Borca,* Paul Scherrer Institute, Switzerland, *P.A. Dowben*, University of Nebraska-Lincoln

We have spatially selectively deposited a zwitterion compound from the class of N-alkyldiaminoresorcinones (or 4,6-bis-dialkylaminobenzene-1,3-diones, $C_6H_2(NHR)_2(O)_2$), compounds, where R =C_5H_{11}. These molecules have very strong local dipoles as the delocalized benzene π molecule of the zwitterion "core" loses aromatic character due to the large charge separation. This charge separation provides this type of zwitterion molecule with a large electric dipole moment across the "benzene" like plane. Unlike the ferroelectric materials, the electric dipole of this class of zwitterions when adsorbed on metal surface (and most substrates) is not switchable, which makes these zwitterion compounds more like an electret. We have been able to demonstrate that at least one of this class of zwitterion compound will selective adsorb from solution on periodically poled lithium niobate substrates using infra-red spectra-microscopy. The spatial localization zwitterion on lithium niobate suggests that the ferroelectric poling of lithium niobate either alters the surface chemistry of lithium niobate or that there is some dipole-dipole interaction between the substrate and the zwitterion. We believe the interaction is an interface effect as no alteration in the bulk properties has been observed from spatially resolved near edge X-ray adsorption fine structure (NEXAFS) of the bulk properties. The spatial zwitterion structure is consistent with the periodically poled lithium niobate structure. Crystals of periodically poled lithium niobate (PPLN) with congruent composition (Crystal Technologies) were used as deposition templates. A periodic domain structure (period of ~28 µm) was fabricated by depositing a photoresist mask on the +c sample face and by applying a voltage of 10 kV through a fixture with an electrolyte solution. The mask was removed after poling by means of chemical-mechanical polishing leaving behind a bare ferroelectric surface, prior to the exposure to the zwitterion molecular solution.

In Situ Microscopy and Spectroscopy: Interfacial and Nanoscale Science Topical Conference
Room: C4 - Session IS+AS-FrM

In-Situ Microscopy and Spectroscopy: Dynamic Nanoscale Processes
Moderator: C.M. Wang, Pacific Northwest National Laboratory

8:20am **IS+AS-FrM1 In Situ Atomic-Scale Imaging of an Oxide Supported Catalyst during a Redox Change: WO_x / a-Fe_2O_3 (0001)**, ***Z. Feng***, Northwestern University, *J.W. Elam,* Argonne National Lab, *C.-Y. Kim,* Canadian Light Source Inc., *Z. Zhang,* Argonne National Lab, *M.J. Bedzyk*, Northwestern University

Ultrathin metal-oxide layers deposited onto oxide surfaces have wide applications in catalysis and chemical sensing. Supported tungsten oxides are among these. If the atomic-scale geometrical and electronic surface structure of WO_x could be predicted, this would impact our understanding of numerous chemical processes. As a model catalytic system, atomic layer deposition (ALD) grown WO_x on hematite (0001) was used for finding the positions of W with respect to the support lattice and its sensitivity to the reduction-oxidation (redox) cycle. AFM is used to study the surface morphology changes. X-ray fluorescence and in situ X-ray standing waves (XSW) are used in combination to determine the geometric structure changes during the redox reaction. The XSW results for 1/3 ML W show that W cations on the surface occupy different positions in the as-deposited, oxidized and reduced states. The ALD as-depostied W shows strong correlation vertically but no correlation laterally. Oxidization causes the W ordered and they occupy some special adsorption sites. However, in the reduced state, W cations change their adsorption sites. Atomic density maps created from in situ XSW measurements give us direct informaiton for the W cations surface site location. Finally, X-ray photoelectron spectroscopy (XPS) is used to correlate the W oxidation state(s) with the above redox induced structural changes. A model is proposed to explain the reversible geometrical/electronic structure changes during this redox reaction.

8:40am **IS+AS-FrM2 The Surface Kinetics of the Initial Oxidation Stages of Cu Alloys**, *Z. Li*, ***J.C. Yang***, University of Pittsburgh

We are studying the dynamics of the initial and transient oxidation stages of a metal and alloys with in situ ultra-high vacuum (UHV) transmission electron microscopy (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 and temperatures. The addition of a secondary non-oxidizing element, Au, revealed a self-limiting growth due to the depletion of Cu near the oxide island that significantly slows down the oxide growth as well as lead to an unusual dendritic shape, limiting its ability to form a uniform protective oxide. The Cu-Ni alloys show more complex behavior, where the two components are 100% solid-soluble down to ~300°C but Cu2O and NiO show limited miscibility. Nickel oxide, which has the cubic NaCl crystal structure, has a more negative standard free energy of formation than Cu2O, which is simple cubic, and is expected to form more readily. In this case, depending on the environmental pO2, either one or both components of the alloy will oxidize, thus enabling a systematic determination of the effects of compositional and phase development during oxidation. We noted remarkable differences between Cu-Ni oxidation and our past observations of Cu and Cu-Au oxidation: 1) a second rapid nucleation of compact and dense oxide islands occurred and 2) polycrystalline oxides formed, where only cube-to-cube epitaxial Cu2O islands nucleated on Cu (001) and CuAu (001) for all temperatures and pressures studied. The surface segregation of Cu and Ni towards or away, respectively, from the alloy surface during oxidation could disrupt and cause polycrystalline oxide formation. In addition to being excellent model systems for understanding environmental stability of metal alloys, knowledge of the oxidation behavior of Cu-based alloys is also of practical interest in diverse areas, such as electronics, functional oxides and catalysis.

9:00am **IS+AS-FrM3 In-Situ Aberration Corrected Transmission Electron Microscopy**, ***T.C. Isabell***, *J. Brink, B.L. Armbruster, M. Kawasaki*, JEOL USA, Inc. **INVITED**

Few electron optical inventions have revolutionized the TEM/STEM as profoundly as the spherical aberration (Cs) corrector. Characterization of technologically important materials increasingly needs to be done at the atomic or even sub-atomic level. This characterization includes determination of atomic structure as well as structural chemistry. With Cs correctors the sub-Ångstrom imaging barrier has been passed, and fast atomic scale spectroscopy is possible. In addition to improvements in resolution, Cs correctors offer a number of other significant improvements and benefits.

One such benefit is that a larger pole piece gap can be used in the TEM, while still achieving sub-Angstrom image resolution. This means that there is more room around the sample for in-situ experimentation. This opens the door to a whole realm of dynamic experiments, done on a spatial scale never before possible.

There are a few ways in which in-situ experiments in the TEM can be carried out. The TEM can be dedicated to in-situ experimentation and modified to include an environmental cell around the specimen. Through a differential pumping system, the pressure around the sample can be modified and with gas injection systems, the chemistry around the sample can be controlled. Such E-cell TEM systems have existed for years, but recent improvements in design have expanded the usefulness of such systems. Modern E-cell TEMs are capable of not just TEM imaging, but also energy loss spectroscopy (EELS), scanning transmission electron microscopy (STEM) and in some cases energy dispersive spectroscopy (EDS). However, in fully dedicated E-cell TEMs, scanning techniques and EDS may be geometrically limited.

Alternatively, specially designed TEM specimen holders can be used in a conventional TEM for in-situ work. A variety of environmental holders have been developed for these kinds of experiments, including: heating, cooling, straining, and indentation holders; probe holders for electrical measurements; holders with an enclosed environmental cell so that the specimen can be examined under different gases and or liquids; and even holders with an integrated SPM tip for simultaneous TEM/SPM observation of the specimen. MEMS devices are being used for some of these holders to incorporate things such as rapid heating into the specimen holder.[1] These holders can be used to study transport phenomena across interfaces, sintering phenomena in nanoparticles, and elevated temperature studies of catalysts.[2,3]

[1] J. Damiano, D.P. Nackashi and S.E. Mick; Microsc Microanal 14(Suppl 2) 1332, 2008.

[2] M. Briceno, et al., Microsc Microanal 14(Suppl 2) 1336, 2008.

[3] J. Liu, J. Wang, L.F. Allard; Microsc Microanal 14(Suppl 2) 262, 2008.

9:40am **IS+AS-FrM5 Probing Interfacial Atomic and Electronic Structures at Atomic Resolution**, ***J.-M. Zuo***, University of Illinois - Urbana-Champaign **INVITED**

Interfaces are important because they are essential for the function of materials, especially for nanomaterials. New research in oxide thin-films also shows that interfaces can be used to generate new electronic structures. However, interface characterization is always a challenge. Here, I will present our progress in probing atomic structure and electronic structure of interfaces based on aberration corrected scanning transmission electron microscopy and electron energy loss spectroscopy (EELS). Specifically I will cover two topics, one is the epitaxial interface between metal nanocrystals and oxides and the other is atomic scale oxide superllatices. I will illustrate the resolution of the aberration corrected electron microscopy and EELS, and what we have leant from these characterizations.

10:20am **IS+AS-FrM7 Bringing Chemical Reactions to Life: Environmental Transmission Electron Microscopy (ETEM)**, ***B. Freitag***, *D. Stokes, D. Hubert*, FEI Company, The Netherlands **INVITED**

Electron microscopy can provide more than just static observations and characterization of materials. For example, the environmental transmission electron microscope (ETEM) enables the synthesis of materials in the TEM, and allows us to study dynamic behavior under the influence of different gases and temperatures, while maintaining atomic resolution capabilities. By varying the temperature, pressure and composition of the gaseous environment, it is possible to directly interrogate chemical processes using both imaging and spectroscopic techniques. This allows a deep understanding of the mechanisms and kinetics of reactions at the nanoscale, as evidenced by the growing body of literature (see, for example [1-6]).

The most recent addition to the Titan S/TEM family is specifically designed for ETEM studies, with a pressure range of up to 4 kPa (40mbar, 30 torr) of gas at the specimen area and a wide range of temperatures. This special microscope is equipped with a gas sensor and a plasma cleaner and can be operated in non-ETEM mode with the standard sub-Angstrom specifications of a conventional Titan. Figure 1 demonstrates imaging performance for a nitrogen gas pressure p = 500 Pa (5 mbar, 3.75 torr), showing an information transfer of 1.2 Å, obtained for a gold specimen in an aberration-corrected ETEM. In this talk the performance of the ETEM and application results on chemical reactions are presented.

References

[1] R. Sharma and K. Weiss, Microscopy Research and Technique **42**(4) (1998), p. 270-280.

[2] P.L. Hansen, J.B. Wagner, S. Helveg, J.R. Rostrup-Nielsen, B.S. Clausen and Topsoe, H., Science **295**(5562) (2002) p. 2053-2055.

[3] S. Helveg, C. Lopez-Cartes, J. Sehested, P.L. Hansen, B.S. Clausen, J.R. Rostrup-Nielsen, F. Abild-Pedersen and Norskov, J.K., Nature **427** (2004) p. 426-429.

[4] R. Sharma, P. Rez, M. Brown, G.H. Du, and M.M.J. Treacy, Nanotechnology **18**(12) (2007)

[5] S. Hofmann, R. Sharma, C. Ducati, G. Du, C. Mattevi, C. Cepek, M. Cantoro, S. Pisana, A. Parvez, F. Cervantes-Sodi, A.C. Ferrari, R. Dunin-Borkowski, S. Lizzit, L. Petaccia, A. Goldoni and J. Robertson, Nano Letters **7**(3) (2007) p. 602-608.

[6] P.L. Gai, R. Sharma and F.M. Ross, MRS Bulletin **33**(2) (2008) p. 107-114.

11:00am **IS+AS-FrM9 In-situ TEM Investigation of Nanoscale Deformation Mechanisms in Lubricious Thin Films**, ***A. M'ndange-Pfupfu***, *A. Merkle,* Northwestern University, *O. Eryilmaz, A. Erdemir,* Argonne National Laboratory, *L.D. Marks*, Northwestern University

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. 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 nanoscale deformation mechanisms in lubricious thin films, particularly highly-ordered pyrolytic graphite, diamond-like carbon (DLC), and molybdenum disulfide (MoS2). The manner in which the material responds to an applied stress is not only of fundamental interest, but of practical importance as device design shrinks to ever-smaller dimensions.

Using our in-situ approach, we have access to all the instrumentation of the TEM. With HOPG and MoS2, we can use electron diffraction to look at the structural deformations in the graphitic grains as a function of the type and magnitude of applied stress. We have also looked at the phase transformation usually known as graphitization seen in DLC films. 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. By using electron energy loss spectroscopy combined with high resolution imaging, we can look at the effect of film hydrogenation on the speed of the phase transformation, which is useful for both applications and for determining the actual mechanism involved.

11:20am **IS+AS-FrM10 Real-time Observation of Non-diffusive Reactive Spreading of Gold on Silicon**, ***N. Ferralis***, University of California, Berkeley, *F. El Gabaly,* Sandia National Laboratories, *A.K. Schmid,* Lawrence Berkeley National Laboratory, *R. Maboudian, C. Carraro*, University of California, Berkeley

The spreading dynamics of a bilayer gold film propagating outward from gold clusters, which are pinned to the clean Si(111) surface, are imaged in real time using low energy electron microscopy. By monitoring the morphological evolution of the Au-Si interface at fixed temperature, a linear dependence of the spreading radius of the interface as function of time is found. The measured spreading velocities in the temperature range of $800 < T < 930$ K varies from below 100 pm/s to 50 nm/s. We show that the linear time dependence in the formation of the interface between the gold silicide and the clean Si surface is a direct consequence of the large difference in surface energy between the two phases. In atomistic terms, the dynamics of the spreading is reaction-attachment limited, and it appears to be regulated by the structural reconstruction of gold silicide that that takes place at the interface.

Magnetic Interfaces and Nanostructures
Room: C1 - Session MI-FrM

Molecular/Organic Based Magnetism
Moderator: A.N. Caruso, University of Missouri-Kansas City

8:20am **MI-FrM1 Molecular/Organic based Magnetism: New Chemistry, Physics, and Technologies**, ***A.J. Epstein***, The Ohio State University **INVITED**

In recent years a broad range of magnetic and magnetotransport phenomena have been reported for organic semiconductors. Unpaired spins in the p orbitals of organic systems have been shown to yield new physics and be the basis of potential new technologies of broad interest. Organic-based magnets with magnetic ordering temperatures from a few K [1] to > 400 K [2] have been successfully synthesized. In addition, new magnetic phenomena have been discovered including fractal magnetism, photonically controlled magnetism, nanoscale magnetic bubbles, and fully spin polarized magnetic semiconductors[3]. Further, magnetotransport (MR) in magnetic and nonmagnetic organic semiconductors has revealed a host of heretofore unknown spin-dependent phenomena, including 20% change in resistance at room temperature for application of as little as 100 Oe to nonmagnetic organic semiconductors. The room temperature magnetic semiconductors $V[TCNE]_{x\sim2}$, (TCNE ≡ tetracyanoethylene) [2,3] has many new properties such as fully spin polarized energy bands and magnetism from 0 to 400 K and photonic response. The analogue $Fe[TCNE]_x$ forms monolayer thick spin layers that produce ‘spin bubbles’ upon application of a critical field.

These advances in science have prompted interest in the possibility of technologies based on these new materials. These new potential technologies will be discussed with emphasis on organic-based spintronics including tunneling magnetoresistance (TMR) and giant magnetoresistance (GMR) devices and also use of these materials as sensors in the emerging THz range.

This work was supported in part by NSF, DOE, AFOSR, and OSU Inst. for Mater. Res.

[1] S. Chittipeddi, K. Cromack, J.S. Miller, and A.J. Epstein, “Ferromagnetism in Molecular DecamethylferroceniumTetracyanoethenide (DMeFc)(TCNE)”, Phys. Rev. Lett. 58, 2695 (1987).

[2] J.M. Manriquez, G.T. Yee, R.S. McLean, A.J. Epstein, and J.S. Miller,“A Room Temperature Molecular/Organic-Based Magnet”, Science 252, 1415 (1991).

[3] A.J. Epstein, “Organic-based Magnets: Opportunities in Photoinduced Magnetism, Spintronics, Fractal Magnetism, and Beyond”, Mater. Res. Soc. Bull. 28, 492-499 (2003).

[4 V.N. Prigodin, J.D. Bergeson, D.M. Lincoln, and A.J. Epstein, “Anomalous Room Temperature Magnetoresistance in Organic Semiconductors”, Synth. Met. 156, 757 (2006).

[5] T. Francis, O¨. Mermer, G. Veeraraghavan, and M. Wohlgenannt, “Large Magnetoresistance at RoomTemp. in Semiconducting Polymer Sandwich Devices”,New J. Phys. **6**, 185 (2004).

9:00am **MI-FrM3 Tuning Molecule-Mediated Spin Coupling in Bottom-Up Fabricated Vanadium-TCNE Nanostructures**, *D. Wegner, R. Yamachika,* ***X. Zhang***, *Y. Wang,* University of California, Berkeley and Lawrence Berkeley National Laboratory, *T. Baruah,* University of Texas, El Paso, *M.R. Pederson,* Naval Research Laboratory, *B.M. Bartlett, J.R. Long,* University of California, Berkeley, *M.F. Crommie*, University of California, Berkeley and Lawrence Berkeley National Laboratory

We have fabricated hybrid organic/inorganic magnetic molecules based on vanadium atoms and tetracyanoethylene (TCNE) ligands in an atom-by-atom fashion using a cryogenic scanning tunneling microscope. Using tunneling spectroscopy we observe spin-polarized molecular orbitals as well as a structure-dependent Kondo resonance. For complexes having two V atoms, the Kondo behavior can be switched on and off by a minute structural change that leaves the spin-containing orbital essentially unchanged. This can be explained by a tunable, structure-dependent change in the vanadium spin-spin coupling strength through the TCNE molecule, as confirmed by density functional calculations. The present findings offer a new route for designing molecular spin nanostructures with atomic-scale precision.

9:20am **MI-FrM4 Resolving the Interface Magnetism of a Molecule-Based Spin Filter**

J. Brede, S. Kuck, ***G. Hoffmann,*** University of Hamburg, Germany, *P. Lazic, S. Blügel,* FZ Jülich, Germany, *R. Wiesendanger,* University of Hamburg, Germany, *N. Atodiresei*, FZ Jülich, Germany

The use of magnetic molecules opens a gateway to a flexible design of spintronic devices to store, manipulate, and read spin information at nanoscale level. Crucial is the precise knowledge of molecular properties at the interface towards an electrode. Progress into this field relies on resolving and understanding the physics at the relevant interface, the role of individual molecular constituents, and the impact of the atomic environment nearby on molecular properties. Here, we apply spin-polarized scanning tunneling microscopy to resolve the physics of such an interface formed of a magnetic metal-organic molecule adsorbed on a magnetic substrate to observe on an atomic scale the operation of single-molecule spin filter. The experimental data reveal a significant and strongly site dependent localization of spin split states at the interface. To understand the resulting spin-polarization, density functional theory calculations are performed with an extension to describe correlation effects present due to the close proximity of a molecule and a metallic substrate. The results of the joint work are presented and the physical processes at the molecule-electrode interface are discussed.

Acknowledgements: This work was supported by the DFG within the GrK 611 and the SFB 668-A5 and by the European Union in the project “SPiDMe”.

9:40am **MI-FrM5 The Densest Iron Coordination Network Based on Carboxylate Ligands**

D. Ecija*, C. Urban, M. Trelka,* Universidad Autonoma de Madrid, Spain*, C. Marti-Gastaldo, E. Coronado,* ICMOL & Universidad de Valencia, Spain*, J.M. Gallego,* ICMM-CSIC, Spain*, R. Otero, R. Miranda*, UAM & IMDEA-Nano, Spain

Over the last decade there has been a tremendous effort in order to create new kinds of supramolecular organic nanostructures on surfaces, with the prospect of possible catalytic, electronic, optical or magnetic applications. In particular, a lot of attention has been paid to metalorganic coordination networks (MOCNs), with the idea of creating functional metallo-supramolecular arrays on surfaces which combine the properties of their constituent metal ions and ligands.

Following this approach, the chemisorption of small molecules with ending carboxylic acids on metal surfaces has been extensively studied and deprotonation of the acid groups to produce carboxylate groups described [1]. These deprotonated groups can interact strongly with both metal surfaces and metal adatoms (either intentionally deposited or already existing as a 2D background gas that results from the emission of atoms from low coordination sites such as steps and kinks). This metal-to-carboxylate interaction, when properly addressed, leads to the formation of regular patterns of MOCNs. We have deposited oxalic acid, i.e. the smallest possible molecule with two carboxylic groups (C2O4H2), on non magnetic Cu(100) surfaces, both clean and with a small pre-deposited amount of Fe. Scanning Tunnelling Microscopy (STM) shows that moderate annealing of these systems lead to the formation of two different, new MOCNs: a rectangular copper-oxalate network, and a honeycomb iron-oxalate network, where the regularly spaced Fe spins have the smallest distance (5.2 Å) reported up to date, making the Fe-oxalate MOCN a promising system for an in-depth study of their magnetic properties.

[1] S. Stepanov, N. Lin, J. V. Barth, J. Phys.: Condens. Matter 20 (2008) 184002.

10:00am **MI-FrM6 Spatially Extended Kondo Resonance in Magnetic Molecules**

U.G.E. Perera, Ohio University*, H.J. Kulik,* Massachusetts Institute of Technology*, V. Iancu,* Ohio University*, L.G.G.V. Dias da Silva,* Oak Ridge National Laboratory and University of Tennessee*,* ***S.E. Ulloa****,* Ohio University*, N. Marzari,* Massachusetts Institute of Technology*, S.-W. Hla*, Ohio University

Molecules containing transition-metal complexes have great potentials in the emergent fields of spintronics and molecular electronics. Especially, controlling their spin states and spin polarization is a key challenge for future applications. Here, we report an extensive and unusual redistribution of spin density for self-assembled TBrPP-Co [5, 10, 15, 20 –Tetrakis -(4-bromophenyl)-porphyrin-cobalt] molecules adsorbed on a Cu(111) surface as a model system to investigate spin polarization, the effect of molecular orbital in Kondo resonances. The TBrPP-Co molecule has a spin-active cobalt atom caged at the center of porphyrin unit and four bromo-phenyl groups are attached to its four corners. STM imaging shows the molecules with four pronounced lobes. These molecules readily self-assemble and form ordered, ribbon-like monolayer islands on Cu(111), with a preferential growth direction ~7° deviated from the [110] surface directions. We probe the spatially extended Kondo resonance of the molecules by monitoring the effective Kondo temperature with differential conductance (dI/dV) tunneling spectroscopy, finding it much larger on the macro-cycle itself than on the central cobalt atom. The origin of this effect is explained by means of first-principles and numerical renormalization group calculations, highlighting how it is possible to engineer spin polarization and electronic transport by means of adsorption chemistry. This work is supported by the US Department of Energy Basic Energy Sciences grant no. DE-FG02-02ER46012.

10:20am **MI-FrM7 Pressure Dependent Magnetic and Optical Properties of M [TCNE] (MeCN)$_2$X (M= V, Fe, Mn, Co, Ni; TCNE = tetracyanoethylene) Organic-Based Magnets**

K.I. Pokhodnya*, C. Olson,* North Dakota State University*, A. Midgley, M.B. Kruger, A.N. Caruso*, University of Missouri - Kansas City

M-TCNE molecule-based ferrimagnets demonstrate high magnetic ordering temperatures up to 400 K (M = V) due to strong AFM exchange between *d*-electrons of the metal and the anion-radical spin of the TCNE ligand. Magnetic and optical properties of the family of molecule-based 2D magnets [M(TCNE)(NCMe)$_2$] X (M=Fe, Mn, Ni; X=BPh$_4$, FeCl$_4$, SbF$_6$) will be discussed. Classical bonding-sensitive IR spectroscopy has difficulties distinguishing between the bonding and backbonding interactions (possibly mediating the strong superexchange), since their effects on CN bond stretching mode frequencies may cancel each other. In contrast, Raman active n(C=C) modes solely depend on charge transfer to/from the p* antibonding orbital, and thus are only backbonding sensitive. The observed strengthening of the n(C=C) and n(NºC) Raman modes for the compounds with higher T_c suggests the depopulation of the p* orbital and enhanced ligand to metal charge transfer resulting in a hybrid M3*d*-CN ground state with substantial admixture of ligand electron. The observed pressure-induced strengthening of the n(C=C) and n(NºC) Raman modes is in accord with proposed backbonding model. The correlation between the frequency shift (degree of backbonding) and magnitude of T_c from M(T) is established.

10:40am **MI-FrM8 UV/Vis Magnetic Circular Dichrosim of Fe[TCNE]**

S.Z. Janjua*, A.N. Caruso*, University of Missouri - Kansas City

The unoccupied electronic structure of the Fe^{II}[TCNE]$_x$•*z*S (TCNE = tetracyanoethylene; S = CH$_2$Cl$_2$) organic-based magnet has been studied using x-ray magnetic circular dichroism (XMCD) and standard x-ray absorption, but no clear picture of the binding energies nor their spin polarization has been determined. UV/Vis MCD studies have been completed, and will be presented within the ligand to metal charge transfer transition model, as a complimentary and possibly more sensitive means by which the unoccupied electronic structure may be determined. Further, the UV/Vis MCD were conducted to investigate the charge and intervalance transfer from ligand to metal orbital’s.

11:00am **MI-FrM9 Perspectives in Multi-Functional Single-Molecule Magnets and Single-Chain Magnets**

M. Yamashita, Tohoku University, Japan **INVITED**

Recently, the quantum molecular nano-magnets have been attracting much attention from the viewpoints of the basic sciences as well as the applied sciences such as memory storages, quantum computers, etc. So far more than 300 single-molecule quantum magnets have been reported, while about 20 types of single-chain quantum magnets have been reported. They have several interesting themes to be resolved as follows: (1) High blocking temperature, (2) Quantum GMR, (3) Memory storage into one quantum molecule magnet, (4) Quantum computer, (5) Quantum FET, (6) Glauber dynamics, (7) Multi-functionalities, (8) Kondo effect, etc.

As for (1), since the potential barrier of the double wells is defined as DS^2 and $(8J+D)S^2$ for the single-molecule magnets and single-chain magnets, respectively, we must increase the *D*, *S*, and *J* parameters to raise the blocking temperatures of these compounds. However, the control of the parameter *D* is very difficult. Then, we propose the conducting quantum molecular magnets. By the interaction between conducting electrons and localized quantum molecule magnets, the coherence among the quantum molecule magnets is strengthened and then the spin flips are made difficult, resulting in raising the blocking temperature. According to such a strategy, we have synthesized three types of conducting single-molecule magnets such as [Mn$_4$(hmp)$_6$(MeCN)$_2$][Pt(mnt)$_2$]$_6$, [Mn$_2$(5-MeOsaltmen)$_2$(MeCN)$_2$][Ni(dmit)]$_7$(MeCN), and [Mn$_2$(5-Rsaltmen)$_2$][Ni(dmit)$_2$]$_2$. As for (2), since in the quantum molecular magnets, we can create artificially the large spin numbers such as S=10, 20, 30, etc, we can anticipate new quantum GMR phenomena by interacting between large *S* and conducting electrons. According to such a strategy, we try to synthesize a metallic single-molecule magnet. Otherwise, we have a plan to occur a photo-induced phase transition from semiconductor to metallic state in conducting single-molecule magnet. As for (3), we have accessed to one single-molecule magnet of Pc_2Tb by STM. We have a plane to input one memory into one single-molecule magnet and output it from one single-molecule magnet by using spin-polarized STM. We have observed Kondo Effect at 4.8 K in this compound by STS for the first time. As for (7), we have synthesized the single-molecule magnet with photo-induced switching and the single-chain magnet with absorption and desorption of crystal solvents reversibly like a spo

MEMS and NEMS
Room: B3 - Session MN-FrM

Multi-scale Interactions of Materials and Fabrication at the Micro- and Nano-scale
Moderator: M. Metzler, Cornell University

8:20am **MN-FrM1 Using Nonlinearity to enhance Micro/NanoSensor Performance**, ***K. Turner***, University of California, Santa Barbara **INVITED**

Resonant microelectromechanical systems are key building blocks for many microsensor applications, including mass detection, inertial detection and RF filters and timing oscillators. Especially in high-Quality-factor systems, often amplitudes are such that nonlinearities are present. In many applications, these nonlinearities can be significant, and need to be accounted for. In this talk, I will give an overview of a few applications where understanding and cleverly utilizing nonlinearity actually results in improved sensor performance.

Examples including mass sensors and resonant angular rate sensors (Coriolis force sensors) will be used to explain these concepts.

9:00am **MN-FrM3 High-*Q*, In-plane Modes of Nanomechanical Resonators Operated in Air**, ***P. Waggoner***, *C. Tan*, *L. Bellan*, *H. Craighead*, Cornell University

Viscous damping is perhaps the greatest limitation on the applicability of nanomechanical resonant sensors, typically reducing device quality factors by several orders of magnitude when operated in air or liquid as compared to vacuum. In addition to degraded sensitivity due to lower quality factors, the viscous media also effectively adds mass to the sensors, shifting the resonant frequency and further decreasing sensitivity to added mass. In order to achieve real-time, ambient sensing of biological and chemical analytes, a solution to these problems must be achieved. We have fabricated arrays of 90 nm thick mechanical resonators, studied their resonance spectrum as a function of pressure, and found that some higher order resonant modes feature quality factors on the order of 2000 at atmospheric pressure, namely two symmetric, in-plane resonant modes. The side-to-side resonance of these trampoline-shaped resonators was confirmed using finite element analysis and by experimentally exciting device resonance non-uniformly. Even after deposition of a relatively thick polymer layer, the quality factor of the in plane mode in air only decreased slightly, suggesting that functional sensing layers can be used with devices operated in air. These encouraging results open the door for resonant micro- and nanoelectromechanical systems (NEMS & MEMS) to biosensor and chemical sensor applications at atmospheric pressure.

9:20am **MN-FrM4 An Overview of a Simple Fabrication Method for Effective Piezoresistive Transduction of MEMS Resonators**, ***J. Cross***, *B.R. Ilic*, Cornell University, *M. Zalalutdinov*, Global Strategies Group, *J. Baldwin*, *B. Houston*, Naval Research Laboratory, *H. Craighead*, *J.M. Parpia*, Cornell University

We present an overview of studies on a piezoresistive transduction mechanism for detecting MEMS resonator motion. The transduction mechanism is based upon flexure of two fabricated stacked layers of polysilicon, separated by a thin dielectric material. We have used thermal silicon dioxide and LPCVD silicon nitride for dielectric layers. The dielectric material's resistivity can be reproducibly electrically tuned via breakdown to tailor a vertically-oriented piezoresistive transducer between the polysilicon layers. The transduction mechanism is presented analytically, along with examples of non-linear data used to determine the displacement of the resonators. We obtain a gauge factor of approximately 5 with silicon dioxide as the dielectric, which is adequate for direct detection of the resonator motion without amplification or impedance matching. Integrated resonator-transducer devices in various geometries, such as double-clamped beams and cantilevers, have been fabricated using this method and we report on the effectiveness of various geometric parameters as well as various thicknesses and resistances of dielectric layers. As the film stack is composed entirely of CMOS compatible materials, we discuss a fabrication recipe for integrating this transduction mechanism with a conventional CMOS fabrication process. 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-FrM5 Determination of Young Modulus and Density of Thin Films using Nanomechanics**, ***B.R. Ilic***, Cornell University, *S.L. Krylov*, Tel Aviv University, Israel, *H. Craighead*, Cornell University

Material properties of atomic layer deposited (ALD) thin films are of considerable interest to proposed applications ranging from wear resistance to high k-dielectrics in electronic circuits. We demonstrate the ability to simultaneously measure Young's modulus (E) and density (ρ) of 212-215Å ALD hafnia , alumina and aluminum nitride ultrathin films from vibrations ofnanomechanical cantilever beams. The nanomechanical structures were fabricated from a 250nm thick single crystal silicon layer with with varying length and width ranging from 6 to 10μm and 40nm to 1μm, respectively. Our approach is based on an optical excitation and interferrometric detection of in-plane and out-of plane vibrational spectra of single crystal silicon cantilevers before and after a conformal deposition of an ALD thin film. Due to the high degree of conformality, uniform thickness and composition of ALD films, fundamental mode eigenvalues depending on uncertainties in geometrical parameters and clamping compliances of the nanomechanical structures were filtered out. In conjunction with three-dimensional numerical finite element analysis, baseline measurements carried out prior the deposition revealed that while the influence of clamping compliances arising due to the undercut of the sacrificial layer is significant for wider beams, the effect is less pronounced for both, narrower cantilevers and the in-plane vibrational responses. Following the deposition, higher stiffness alumina films ($E>E_{Si}$) showed an increase in the resonant frequency whereas lower stiffness ($E<E_{Si}$) hafnia and aluminum nitride films decreased the natural frequency. From the measured spectral response, material properties were extracted using simple expressions for E and ρ in terms of measured in-plane and out-of-plane frequencies shifts were derived from a model based on an ideally clamped Euler-Bernoulli beam with effective bending stiffness and effective mass per unit length. In-plane and out-of-plane frequency measurements provided two equations required for the extraction of E and ρ without the necessity of knowing material density prior to experiment. Our theoretical and experimental results are in good agreement with the data available in literature and indicate that the suggested approach can be efficiently used for the in-situ material parameters extraction of very thin films incorporated in nano-scale oscillators as well as for combined stiffness-density based material identification and comparative quantitative characterization of the film quality.

10:00am **MN-FrM6 Parametric Excitation of Microstructures by Direct Mechanical Stiffness Modulation**, ***S.L. Krylov***, *Y. Gerson*, Tel Aviv University, Israel, *T. Nachmias*, *U. Keren*, Microsystems Design Center, RAFAEL LTD, Israel

In this work, we report on theoretical and experimental investigation of resonant behavior of a parametrically excited microstructure actuated by a time-varying electrostatic force. Parametric devices typically described by

Mathieu-type differential equations with time-dependent coefficients are attractive for a broad variety of applications such as mass sensors, dynamic electromechanical amplifiers or inertial sensors due to the ability to generate resonant responses in relatively wide band of excitation frequencies as well as sharp transition between low-amplitude to large-amplitudes responses. In electrostatically actuated MEMS devices, parametric

excitation arises mainly as a result of nonlinearity of electrostatic forces combined with periodic time dependencies of the actuation voltage as well as for geometrical reasons or due to kinematic excitation.

In this work we implement direct mechanical stiffness modulation by means of a periodic tensile force applied along suspension flexures. The frame-type structure is realized as a pair of cantilever (clamped-guided) beams connected at their ends by a rigid link. The electrostatic actuation force applied to the rigid link by a parallel-plate electrode connected to an AC voltage source results in a periodic tensile force within the beams and consequently in periodic structural stiffness modulation and mechanical parametric excitation of the structure. Combination of compliant cantilever-type suspension with lateral motion in the direction parallel to the electrode results in large resonant amplitudes and higher quality factors while high axial stiffness in the direction of the force application prevents undesirable pull-in instabilities. The devices were fabricated from single crystal silicon using silicon on insulator (SOI) substrates and deep reactive ion etching (DRIE) process. The devices were excited electrostatically in the vicinity of the 2:1 subharmonic (parametric) as well as primary resonances and large resonant responses were registered. The lumped model of the device consists of a rigid link undergoing electrostatic loading as well suspension flexures modeled as geometrically nonlinear massless beams. Experimental resonant curves as well as stability regions boundaries built by means of video acquisition and image processing are in good agreement with the results provided by the model. Theoretical and experimental results indicate that the suggested actuation approach have clear functional advantages and could be efficiently used for excitation of various types of microdevices where resonant operation combined with robustness and large vibrational amplitudes are desirable.

10:20am **MN-FrM7 Fabrication of Overhanging Magnet-Tipped Cantilevers for Nanoscale Scanned-Probe Magnetic Resonance***, **J.G. Longenecker**, S.A. Hickman,* Cornell University*, L.E. Harrell,* United States Military Academy*, J.A. Marohn*, Cornell University

Mechanical detection of magnetic resonance opens up exciting possibilities for characterizing soft materials at nanometer-scale, and potentially atomic-scale, resolution. Scanned-probe detection of single-spin electron paramagnetic resonance has been demonstrated. Proton images exhibiting 4 nm resolution have recently been acquired via magnetic resonance force microscopy (MRFM), albeit in an experiment with the sample glued to the cantilever. With the goal of pushing proton imaging resolution beyond 4 nm in a true scanned-probe experiment capable of imaging potentially any thin-film sample, we have taken up the challenge of fabricating attonewton-sensitivity cantilevers with integrated nanorod magnetic tips.

Since the force exerted on the cantilever, per spin, is proportional to the field gradient from the magnetic tip, achieving single proton sensitivity requires reducing the magnetic nanorod diameter to below 50 nm. In the most sensitive scanned-probe magnetic resonance measurements to date, a magnetic particle was manually affixed to the cantilever and the particle diameter reduced to ~150 nm by focused-ion-beam (FIB) milling. Unfortunately, FIB is a serial process and it is difficult to see how FIB milling can be used to make MRFM tips smaller than ~150 nm due to ion-beam damage limitations.

We demonstrate a method for batch-fabricating attonewton-sensitivity silicon cantilevers with integrated nickel tips having critical dimensions of 70 nm. The magnets are patterned by electron-beam lithography and can therefore potentially be made even smaller. The overall fabrication protocol involves thirty-eight carefully-integrated processing steps, including three electron beam lithography steps and two isotropic etching steps. A crucial feature of our cantilever design is that their narrow magnetic tip overhangs the leading edge of the cantilever by up to 400 nm, which minimizes extraneous force and frequency noise in the MRFM experiment known to arise from interactions of the cantilever charge with fluctuating electric fields and field gradients in the sample. Cantilever magnetometry indicates that the tips are nearly fully magnetized. We will detail ongoing work to develop cobalt tips, to push magnet critical dimensions to less than 50 nm, and to study the chemical structure of the tips using high-resolution transmission electron microscopy.

10:40am **MN-FrM8 Nanoscale Resonant Mass Sensors Containing Nanofluidic Channels***, **R.A. Barton**, B.R. Ilic, S.S. Verbridge, H. Craighead, J.M. Parpia*, Cornell University

The ability of nanomechanical resonators to sense mass in a liquid environment is compromised by a large dissipation of energy to the surrounding liquid. One way to overcome this problem is to deliver analytes in solution to the resonator via an embedded fluidic channel, while surrounding the resonator itself with vacuum. Previously, this technique has been applied to detect mass from solution with roughly femtogram precision, but it has never been applied with the sensitivity required to detect single biomolecules. In order to enable studies in the regime of attogram analyte mass, we have designed and fabricated resonators that contain nanofluidic channels. We optically actuate and detect mechanical resonance of the channels and estimate from their frequency and quality factor that they will be able to detect mass with sub-attogram precision. We anticipate that these devices will be useful for sensing and for studies of single large biomolecules.

11:00am **MN-FrM9 Spectroscopic Investigations of XeF_2 Chemistry with Si and Mo Layers on Al Substrate***, **J.-F. Veyan**, K. Roodenko, Y. Gogte,* University of Texas at Dallas*, X.-M. Yan,* Qualcomm MEMS Technologies, Inc.*, Y. Chabal*, University of Texas at Dallas

Etching sacrificial material during MENS and NEMS manufacturing constitute an important processing step. XeF_2 is a commonly used chemical etchant because of its selective interaction with pure compounds and their oxides. Practically, realistic systems are characterized by multicomponent films with interfaces, and side reactions have to be taken into account in the study of the complex chemistry taking place during the etching process. We have studied XeF_2 etching of pure Silicon, pure Molybdenum, and Molybdenum deposited on Silicon oxide and Al substrates, in pressures consistent with industrial conditions (~ Torr range) using in-situ time-resolved IR reflection spectroscopy and ex-situ XPS.

We find that Si and Mo react with XeF2 in very different ways. For Si, F atoms penetrate deep inside the Si lattice, for Mo they stay at the surface. These differences greatly affect the etching kinetics, involving bulk-controlled etching process for Si, and a surface controlled etching for Mo.

After XeF_2 etching and removal of Mo and Si films deposited on Al substrates, the surfaces exhibit residual molybdenum (oxy) fluoride and silicon oxide layers. F1s core level spectra indicated excess fluorine atoms on all surfaces. CF_x contaminations have been found on Si/Al and on Mo/Al surfaces after etching, but not on bare Al substrates, even after XeF_2 exposures. The stability of etched surfaces is also studied.

11:20am **MN-FrM10 Cryogenic Inductively Coupled Plasma Etching for Fabrication of Tapered Through-Silicon Vias***, **A. Kamto**,* The University of Alabama*, R. Divan, A.V. Sumant,* Argonne National Laboratory*, S.L. Burkett*, The University of Alabama

Vertical interconnects pose an interesting method for heterogeneous integration of electronic technologies allowing three-dimensional (3D) stacking of Microelectromechanical systems and integrated circuit device components [1, 2]. The vertical interconnects, referred to as through-silicon vias (TSVs), begin with formation of blind vias in silicon that are eventually exposed by mechanically lapping and polishing the wafer backside. Inductively coupled plasma (ICP) etching using SF_6/O_2 gas chemistry at cryogenic temperatures has been investigated as a way to form vias with a tapered sidewall. The point in creating a controlled taper is so that subsequent thin films can be deposited along the sloped sidewall lining the via with insulation, barrier, and seed films. This tapering is necessary if the via lining processes do not provide adequate conformal coverage, a common problem for conventional low temperature deposition processes. In our process for lining vias, plasma enhanced chemical vapor deposited (PECVD) silicon dioxide is used to insulate vias from the surrounding silicon. After insulation, thin films of Ti and Cu are sputter deposited. Ti provides protection from copper migration while the Cu acts as a seed layer for the electrodeposition step. After etching and lining, the vias are filled by reverse pulse plating of Cu. Vias are 20 - 25 μm in diameter and etched using a photoresist mask. The effect of changing gas flow rates, chamber pressure, RF forward power, ICP power, and substrate temperature on etch rate, via profile, and sidewall morphology will be presented. These parameters are critical in optimization of an etch process for vias of specific dimensions to be used in 3D integration.

This work is supported by the College of Engineering at the University of Alabama. 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 No. DE-AC02-06CH11357.

References:

[1] N. Ranganathan, D. Y. Lee, L Ebin, N. Balasubramanian, K. Prasad and K.L. Pey, *J. Micromech. Microeng*. 18, 115028 (2008).

[2] 3D Integration: Technology and Applications, P. Garrou, P. Ramm, and C. Bower, Editors, Vol. 1, 2, *Wiley Press* (2008).

Plasma Science and Technology
Room: B2 - Session PS-FrM

Plasma Science for Medical and Biological Applications
Moderator: J. Hopwood, Tufts University

8:20am **PS-FrM1 Positive Streamers Propagating Inside Bubbles in Liquids***, **N.Yu. Babaeva**, M.J. Kushner*, University of Michigan

Pulsed discharges in liquids are often in the form of streamers. In most cases, streamers do not directly propagate through the liquid phase. Rather breakdown occurs inside bubbles and near gas–liquid interfaces. Often bubbles are purposely injected to facilitate breakdown. Such discharges have been extensively studied for their use in water treatment, surgery, decontamination and sterilization. Recent experiments have shown that streamers often preferentially propagate along the surface of a bubble immersed in a liquid instead of propagating along the axis of the bubble. In this talk, we discuss results from a computational investigation of the propagation of streamers inside bubbles immersed in liquids. We show that dielectric constant of a liquid determines patterns of streamer propagation. The model, *nonPDPSIM*, is a 2-dimensional simulator executed on an unstructured mesh in which Poisson's equation for the electric potential, and transport equations for charged and neutral species, and electron temperature, are solved. Radiation transport and photoionization are included by implementing a Green's function propagator. A bubble of humid air, $N_2/O_2/H_2O = 55/15/30$ at atmospheric pressure is placed at the tip of a positive corona discharge immersed in a liquid of specified conductivity, σ, and permittivity, $\varepsilon/\varepsilon_0$. The bubble radii are 0.45 - 0.9 mm. We found that for low values of σ and $\varepsilon/\varepsilon_0$ the streamer propagates along the axis of the bubble. For large values of σ and $\varepsilon/\varepsilon_0$ the streamer propagates along the surface of the bubble. For essentially non-conducting liquids, the transition between axial and surface-hugging streamers occurs at $4 < \varepsilon/\varepsilon_0 < 8$, depending on the size of the bubble and voltage. Increasing conductivity lowers the value of $\varepsilon/\varepsilon_0$ at which the streamer becomes surface-hugging. These trends largely result from the refraction of the electric field by the curved interface of the bubble in the presence of a diverging electric field. The final pattern of the streamer path is additionally a function of bubble size and its position relative to the tip of the electrode, applied voltage and polarity.

8:40am **PS-FrM2 Atmospheric Plasma for the Degradation of Pollutants : The Promoting Effect of Water**, *S. Al Takriti, J.M. Giet,* Université Libre de Bruxelles, Belgium*, C. Pierard,* ArcelorMittal Research Liege, Belgium*, **F. Reniers***, Université Libre de Bruxelles, Belgium

Atmospheric plasmas have been used for a long time for the degradation of volatile organic compounds (VOC). In this study we focus on the degradation of non volatile organic compounds, like hexadecane and hexachloropropene, using an oxygen containing atmospheric plasma.

The kinetics of the reactions was followed by mass spectrometry, by tracking the m/z signal of the production of carbon dioxide.

The pollutants were degraded in a dielectric barrier discharge plasma chamber, operating at frequencies between 10 and 20 kHz, and at voltages between 1 and 4 kV. The plasma gas was either pure oxygen, or a helium/oxygen mixture. The promoting effect of water was studied by adding controlled amounts of water vapour to the gas mixture.

Optical emission spectrometry was used to characterize the plasma gas phase. More specifically, the oxygen emission lines, and the OH bands were followed, as a function of the plasma parameters.

It is shown that the degradation efficiency increases with the charge delivered in the plasma, as well as with the oxygen content.. A correlation is established between the oxygen OES emission line and the carbon dioxide production, for plasmas containing no water. For water containing plasmas, the oxygen line decreases, whereas the carbon dioxide production increases. The decrease of oxygen is interpreted in terms of consumption of the oxygen radical by water molecules to create hydroxyl groups, which are responsible for the increase of the degradation of the organic molecules. A simple global mechanism is proposed.

Acknowledgements : this work is funded by the IAP "physical chemistry of plasma-surface interactions - PSI" program from the Belgian Federal Government

9:00am **PS-FrM3 Challenges in the Numerical Simulation of the Plasma-Biomaterial Interaction**, ***Y. Sakiyama**, D.B. Graves*, University of California, Berkeley **INVITED**

Nonthermal atmospheric pressure plasmas have received considerable attention in recent years. One emerging and promising application is the biomedical field. A wide variety of investigators have already demonstrated various biomedical effects of nonthermal plasmas, including sterilization/disinfection, blood coagulation, wound healing, tissue regeneration, etc. [1] The mechanisms of the plasma-biomaterial interaction are however only poorly understood. A central scientific challenge is therefore how to answer the question: “What plasma-generated species or plasma-created electric fields and currents, or any other effects of the plasma, are responsible for the observed biological effects?” Our modeling efforts are motivated by this question.

We have focused on the RF-excited plasma needle at atmospheric pressure and developed fluid models using the finite element method. Our simulation model successfully reproduced various experimental observations. For instance, our two dimensional model demonstrated that the plasma needle operates in two discharge modes: the corona-mode under low power condition and the glow-mode under high power condition. [2] The model showed that the plasma needle discharge strongly depends on the electrical properties of treated materials. [3] Also, we found that the ring-shaped emission pattern observed during bacteria treatment[4] was due to back-diffusion of air and Penning ionization and excitation of N_2 from He metastables. [5] Furthermore, results from a more complete model including humid air chemistry indicate that plasma-air interaction creates various neutral species via electron impact reactions near the treated materials. Those reactive neutrals (e.g. O, OH, NO) appear to have significant effects in the inactivation processes by the plasma needle.

In this talk, we will briefly review recent progress in biomedical applications of gas plasmas. Then, our modeling results are discussed in detail.

1 G. Fridman *et al.*, Plasma Process. Polym. **5** (2008) 503.

2 Y. Sakiyama and D. B. Graves, J. Phys. D **39** (2006) 3644.

3 Y. Sakiyama and D. B. Graves, J. Phys. D **41** (2008) 095204.

4 J. Goree *et al.*, J. Phys. D **39** (2006) 3479.

5 Y. Sakiyama and D. B. Graves, Plasma Sources Sci. Technol. **18** (2009) 025022.

9:40am **PS-FrM5 A Novel Way of using Plasma to Sterilize Objects for Use in Medical, Food or Pharmaceutical Applications**, ***N.B. Koster**, F.P. Wieringa, R. Koops*, TNO Science and Industry, Netherlands

From literature it is known that plasma is capable of sterilizing objects. A number of the great advantages of plasma sterilization is that it is relatively cool and that it also has a cleaning action besides the sterilisation process. A disadvantage of plasma sterilization is that for a good process the object has to be placed in a reactor and after the process is completed the object has to be packed in an enclosure and sealed. This is a possible source of cross contamination due to handling and exposure to the environment. We will present a novel way of using plasma’s to sterilize an object without this disadvantage. This process is called Plasma in a Bag (PiB) and has the benefit that the object is packed and sealed from the environment before the process starts and requires no handling after the sterilization process has finished. Also the way of packing enables the user to see that the enclosure is still intact and that the integrity of the object remains valid even after a long shelf life. We will show results on the efficiency of the process for several pathogens at different plasma conditions. This new process enables the use of new materials and electronics for medical applications or can replace a number of existing sterilisation techniques.

10:00am **PS-FrM6 Patterned Growth of Cells and Biomolecules using a Microplasma Printing System**, *E. Yildirim-Ayan,* Drexel University*, **D. Pappas***, Army Research Laboratory

A versatile system called *micro-plasma integrated cell/biomolecule printing system* is described. This system enables the creation of patterned cells/biomolecules on various substrates without using any masks, master stamps or chemical treatments. The system operation is based on the integration of two techniques, namely microplasma patterning and cell/biomolecule printing. In microplasma patterning, an atmospheric pressure low-temperature microplasma is generated with a dielectric barrier discharge (DBD) plasma setup consisting of a micro-second pulsed power supply and electrode system. Through *micro-plasma integrated cell/biomolecule printing system,* we can create chemically and physically predesigned micropatterns and print the cells/biomolecules on designed pattern with precise spatial positioning.

In this study, the authors patterned mouse osteoblast cells on ultra high molecular weight polyethylene films. An O_2/He mixture was used as the working gas for the ignition of a micron-sized discharge. The microplasma nozzle with a tip of 30 μm was navigated on a straight line with a 2mm/s speed to create the micropattern. The physicochemical properties of the microplasma patterned surface were examined by Scanning Electron Microscopy (SEM) and X-Ray Photoelectron Spectroscopy (XPS). The SEM data showed that the dynamic microplasma treatment results in an increase of the surface roughness. The surface morphology was changed along the microplasma treated line while the rest of the substrate remained unaffected. The XPS data showed that the atomic concentration of oxygen increased from 5% for the as-received polyethylene film to 18% for the center of the microplasma treated line. Following the micropatterning, mouse osteoblast cells were deposited uniformly on the substrate to determine the effect of microplasma patterning on cell attachment. The biological characterization has been done by live/dead assay where mouse osteoblast cells were labeled and imaged using fluorescence microscopy. The data showed the attachment and survival of the cells strictly along the plasma activated line. With these observations, it is viable to print the cells and dictate their shapes in predetermined locations and arrays through *micro-plasma integrated cell/biomolecule printing system*.

10:20am **PS-FrM7 How Does the Chemical Equilibrium in the Vaporous Phase Influence the Surface Properties of Poly-Parylenes?**, *T.H.T. Huber, F. Schamberger,* **G. Franz**, Munich University of Applied Sciences, Germany

The properties of deposited polymeric films strongly depend on the density and the state of excitation of the species in the vaporous phase which determine the degree of consecutive reaction paths covering the bandwidth between volume polymerization and surface polymerization. According to Yasuda, the former reaction mainly causes roughened fine-grain deposits, whereas smooth and shiny layers can be generated easily by the latter one [1]. For chemical vapor deposition, the main parameters are gas flow, number density (degree of rarefaction) and gaseous temperature which are extended by a row of additional parameters in plasma-activated processes, beginning with the (absorbed) plasma power and terminating with the delicate parameters obtained by diagnostic tools. These changes in the reaction mechanism were extensively studied for the biocompatible molecule parylene (*p*-xylylene) which is already deposited on stents for tribological purposes and is intended to cover the inner surface of artificial bladders [2]. We investigated the deposition two types of pure parylene (type N: non-substituted, and type C: substituted by one Cl atom), diluted with different amounts of argon, and a reactive alternative by adding oxygen [3]. The *in-situ* methods are energy-dispersive mass spectrometry and Langmuir probe analysis which have been correlated with *ex-post* measurements of the film quality: contact angle (surface energy) and the morphology, but most prominent the content of the aromatic species in the volume of the layer which goes down not unexpected with growing plasma power. Adding oxygen opens the window to a hydrophilic response of the surface. With the knowledge of densities of the dimeric precursor, the monomeric species, and the electron density, we modeled the chemical equilibrium of dissociation, and from the density of the aromatic compounds in the layer, we could follow the track of "safe" polymerization and could also describe the ranges for volume polymerization and surface polymerization [4].

[1] H. Yasuda: *Plasma polymerization*, Academic Press, New York (1985)

[2] G. Franz, F. Rauter, S. Dribinskiy, JVSTA, to be published

[3 K.G. Pruden, K. Sinclair; J. Polymer Sci. **A41**, 1486 (2003)

[4] G. Kokkoris, V. Constantoudis, P. Angelikopoulos, G. Boulousis, E. Gogolides; Phys. Rev. **B76**, 193405 (2007)

10:40am **PS-FrM8 Synthesis of Polystyrene and Sulfonated Polystyrene Thin Films by Atmospheric Pressure Plasma Enhanced Chemical Vapour Deposition**, ***D. Merche***, Université Libre de Bruxelles (ULB), Belgium, *C. Poleunis, P. Bertrand,* Université Catholique de Louvain (UCL), Belgium, *M. Sferrazza, F. Reniers*, Université Libre de Bruxelles (ULB), Belgium

Thin coatings of pp-PS and pp-sulfonated PS were synthesized by "Plasma Enhanced Chemical Vapour Deposition" (PECVD) in a home-built "Dielectric Barrier Discharge" (DBD) system near atmospheric pressure. Styrene (C_8H_8) and trifluoromethane sulfonic acid (CF_3SO_3H) monomers were used as precursors and were introduced in the discharge using a flux of Ar or He. An atmospheric RF plasma torch was also used for PS deposits. It consists of two closely spaced perforated metallic electrodes. The process gas is Ar. The precursor (styrene vapour) was introduced into the plasma downstream of the electrodes (afterglow). The polymers were deposited on various substrates (PTFE, HDPE, stainless steel, glass, and silicon wafer) and were characterized by FTIR, XPS, SSIMS, WCA, AFM and optical microscopy. The plasma phase was studied by OES.

The pp-sulfonated PS films obtained by plasma copolymerization could present interesting properties as electrolyte membrane for miniaturized fuel cell applications (Polymer Electrolyte Membrane Fuel Cell- PEMFC) using H_2 or CH_3OH (Direct Methanol Fuel Cell-DMFC). CF_3SO_3H allows introduce the sulfonic acid groups for proton conductivity in the membrane whereas the styrene constitutes the backbone of the membrane.

The major features that characterize PS are present in the FTIR, XPS and SSIMS spectra, although some differences between pp-PS films and their conventionally polymerized counterparts are observed (like oxygenation during or after deposition due to the atmosphere environment, branching, degree of cross-linking, and unsaturations). According to the WCA and XPS results, the pp-PS films deposited by the RF plasma torch (placed in a plexiglass chamber) are more oxygenated than those deposited by the DBD operated in a much more controlled atmosphere [1]. The chemical structure of the deposited coatings was investigated by FTIR and TOF-SSIMS as a function of the nature of the carrier gas. The pp-PS films synthesized in the presence of Ar (for both processes) exhibit more branching, more unsaturations, a higher degree of cross-linking, and a lower density of aromaticity than pp-PS synthesized with He as the main plasma gas.

The influence of the nature of the carrier gas, and of the discharge voltage and the ratio of the partial pressures of the monomers on the sulfonic content (therefore on the degree of fragmentation of the CF_3SO_3H monomer) for both carrier gases was investigated for pp-PS sulfonated by XPS, SSIMS and FTIR.

[1] D. Merche, C. Poleunis, P. Bertrand, M. Sferrazza, F. Reniers, *IEEE Transactions on Plasma Science* (2009), Under Press, Available online on http://www.ieeetps.org/

11:00am **PS-FrM9 Functionalization of Wood Surfaces in the Afterglow of an Atmospheric Pressure Dielectric Barrier Discharge**, ***J. Prégent***, Université de Montréal, Canada, *F. Busnel,* Université Laval, Canada, *V. Blanchard,* FPInnovations-Division Forintek, Canada, *L. Stafford*, Université de Montréal, Canada

The use of wood products in architectural or exterior applications is often limited by the short durability of these products and the fast deterioration of their appearance. Several waterborne coatings aimed at preserving the wood properties have been developed but these coatings are often characterized by poor adhesion on wood surfaces. To improve adhesion, we investigated modification of the surface properties of wood samples following their exposition to the afterglow of an atmospheric pressure dielectric barrier discharge in N_2/O_2 mixtures. The surface energy divided into a dispersive (non-polar) part, γ_{DS}, and a polar part, γ_{PS}, was determined by means of contact angles measurements. For polar sugar maple samples, γ_{PS} decreased from 78.5 mJ/m^2 before treatment to 59.0 mJ/m^2 after N_2 plasma exposure. γ_{PS} further decreased with the introduction of O_2, reached a minimum value of 31.2 mJ/m^2 at 85%N_2-15%O_2, and then increased until it reached its untreated value in a pure O_2 plasma. The dispersive component showed the opposite behavior, going from 3.3 mJ/m^2 before treatment to 24.4 mJ/m^2 after exposure to the 85%N_2-15%O_2 plasma. On the other hand, no modification was observed for black spruce, probably because untreated samples already had a large dispersive component. Optical emission spectroscopy (OES) was used to understand the change in plasma properties leading to the observed variation of γ_{PS} and γ_{DS}. The gas temperature determined using the second positive system of N_2 ($C^3\Pi_u$ $v'=0$ – $B^3\Pi_g$ $v''=2$) was 320 ± 20 K and showed no trend with O_2 concentration, thus ruling out variations due to thermal effects. Significant NO ($A^2\Sigma^+$ - $X^2\Pi$) emission in the 225-305 nm range was observed in pure N_2 plasmas. However, these bands disappeared with the introduction of O_2, indicating that UV photons are not the prominent species driving the observed decrease in surface polarity. We also observed a strong increase of the N_2^+ ($B^3\Sigma_u$ $v'=0$ - $X^2\Sigma_g^+$ $v''=0$) to N_2 ($C^3\Pi_u$ $v'=0$ – $B^3\Pi_g$ $v''=2$) bandhead intensity ratio with increasing O_2 concentration. Such behavior is usually ascribed to an increase signature of the early afterglow and thus to an increase in the erosion rate of polymer surfaces [1]. In pure N_2 plasmas, one expects N grafting to form nitrogen-containg groups which are likely to promote non-polar bonding [2]. As only a moderate decrease of γ_{PS} was observed in pure N_2 and no change was observed in pure O_2, it is believed that a combination of N grafting and surface erosion by oxygen atoms is required to achieve maximum modification of the surface polarity.

[1] M.K. Boudam et al., J. Phys D. **40**, 1694 (2007)

[2] S. Vallon et al., J. Adhes. Sci. Technol. **10**, 1287 (1996)

11:20am **PS-FrM10 Combination of Bio-template and Ultimate Top-down Etching Processes for Defect-free, High Density, Size-controlled and Excellent Uniform Si-Nanostructure for Ideal Quantum Effect Devices**, ***M. Igarashi***, *C. Huang,* Tohoku University, Japan, *M. Takeguchi,* NIMS, Japan, *S. Horita,* JAIST, Japan, *Y. Uraoka, T. Fuyuki,* NAIST, Japan, *I. Yamashita,* Panasonic Co., Ltd. and NAIST, Japan, *S. Samukawa*, Tohoku University, Japan

Nanometer-scale structures such as quantum dots (QDs) have been widely studied because they have potential applications to the development of quantum effect devices, such as single electron transistors, quantum dot lasers and quantum dot solar cells. To realize quantum dots, the fabrication of defect-free, size-controlled and uniform sub-10-nm-scale structures is needed. However, it is difficult for conventional optical lithography and plasma etching processes to satisfy these requirements.

In this study, we proposed a novel nanofabrication process for the fabrication of nanostructures, which combines a biomaterial template, radical etching and neutral beam etching (NBE). We fabricated silicon nanodisks (disk-shaped silicon nanostructures with diameters of about 10 nm on a very thin silicon oxide film) by using a ferritin iron core as etching mask and Cl NBE. Additionally, we succeeded in precisely controlling the nanodisk diameter by using surface treatment of NF_3 gas + hydrogen radicals (NF_3 treatment). The surface oxide thickness and its removal conditions greatly affected the fabricated nanodisk diameter. It was notable that the coulomb staircases of nanodisk structures were obtained with a conducting AFM probe at room temperature. The successful fabrication of Si nanodisk should be attributed to the defect-free etching process that involved our neutral beam. Our new process is very useful to fabricate defect-free and size-controlled nanostructure for ideal quantum effect devices.

Surface Science
Room: M - Session SS1-FrM

Nanoclusters, Organics and Beam Induced Chemistry
Moderator: J. Zhou, University of Wyoming

8:20am **SS1-FrM1 Site-specific Adsorption of C60 on Au(111)**, *X. Zhang, L. Tang,* ***Q. Guo***, University of Birmingham, UK

The well-known herringbone reconstruction of the Au (111) surface consists of a regular array of line dislocations, which may act as nucleation sites for metals or organic materials [1, 2]. In this study, we reveal for the first time the selective adsorption of C60 molecules at the elbow sites on Au(111). Deposition of submonolayer of C60 molecules onto a Au(111) surface at room temperature usually leads to the co-existence of three structures [3]. In recent experiments we observed site-selective adsorption of individual C60 molecules, which show an obvious preference for nucleating at the elbows of the x type dislocation lines. As coverage increases, compact C60 islands are observed to form on the FCC regions between two neighboring C60 molecules. Interestingly, only about 50% of the elbow sites are active in mediating the formation of these nanometre sized C60 islands. The observed site-specific adsorption and nucleation is interpreted based on findings from high resolution STM imaging which reveals the atomic scale structure of the surface defects around the elbow sites.

Another site-selective adsorption phenomenon was observed after depositing C60 moleules onto parallel gold stripes (gold-fingers) [4], which were fabricated from monoatomic gold steps by high tunnelling current STM scanning. These gold-fingers have different kinds of microfacet ({111} and {100}) on their two parallel steps. The C60 moleules prefer to adsorb on the less stable {100} steps and form close packed islands, while the {111} steps only have their FCC regions been occupied by the molecules. Besides the energy difference, the different underlying herringbone patterns of the two steps may also be a key factor leading to site-selective adsorption to the gold fingers.

References:

1. I. Chado et al., Appl. Phys. Lett. 226 (2004) 178.
2. T. Yokoyama et al., Nature 413 (2001) 619.
3. X. Zhang, R.E. Palmer and Q. Guo, Surf. Sci. 602 (2008) 885.
4. Q. Guo, F. Yin and R.E. Palmer, Small 1 (2005) 76-79.

8:40am **SS1-FrM2 Epitaxial Growth of Organic Nanocrystals with Antiferroelectric Stacking**, ***M. Trelka***, *A. Medina, C. Urban, C. Claessens,* Universidad Autonoma de Madrid, Spain, *R. Otero,* UAM & IMDEA-Nano, Spain, *J.M. Gallego,* ICMM-CSIC, Spain, *T. Torres,* Universidad Autonoma de Madrid, Spain, *R. Miranda*, UAM & IMDEA-Nano, Spain

Organic nanoparticles display size-dependent absorption and fluorescence bands and single photon emission. The detailed understanding of these effects is hindered by the difficulty in the synthesis of organic nanocrystals, i.e. organic nanoparticles with an ordered molecular arrangement. A possibility that remains mostly unexplored is the synthesis of such nanocrystals on solid surfaces. In the same way in which crystalline inorganic nanodots can be epitaxially grown on suitable substrates under conditions in which 3D Volmer-Weber growth takes place, an organic system could in principle be devised such that the growth of crystalline 3D islands sets in before the completion of the first monolayer. In practice, however, for organic adsorbates deposited on inorganic substrates intermolecular interactions are much weaker than molecule-substrate interactions, thus promoting a layer-by-layer growth mode, and preventing the fabrication of isolated 3D nanocrystal.

Here we show that, upon deposition of cone-shaped subphthalocyanine (SubPc) molecules on Cu(111), isolated triangular nanocrystallites up to 3 ML high appear on the surface before the completion of the first monolayer. The different molecular layers show an alternating or antiferroelectric (AF) stacking of the molecular dipole moments. The structure of such nanocrystals can be explained by the joint effect of electrostatic (dipole-dipole) and dispersive (π-π) interactions. Although 1 ML-thick islands can also be found on the surface, the molecular arrangement in these areas is different from the geometry of the 1st-layer molecules in the crystallites. We suggest that the formation mechanism of the organic nanocrystals is related to the existence of two different adsorption geometries, cone-up and cone-down, each of which sits on different molecular layers placed at different distances from the surface upon crystallite formation.

9:00am **SS1-FrM3 Trapping Dynamics on Complex Surfaces: Organic Thin Film Growth on Surfaces Terminated with Self-Assembled Monolayers**, ***T.V. Desai***, *A.R. Woll, S. Hong, K.J. Hughes, J.R. Engstrom*, Cornell University

A significant challenge in fabricating organic thin film transistors is that of controlling and understanding the properties of the interface between the organic semiconducting layer and the dielectric. It has been observed that charge transport can be affected significantly by chemically altering the dielectric surface with self-assembled monolayers (SAMs). However, the effects of the molecular scale interactions between the organic molecule and the substrate remain unclear. Diindenoperylene (DIP) is a promising candidate for applications in organic thin film electronics owing to the ability to form highly ordered films with excellent electrical properties. Here, using supersonic molecular beam techniques and *in situ* real time synchrotron X-ray scattering, we have examined the adsorption dynamics of DIP on silicon dioxide (SiO_2) and SiO_2 modified with a number of SAMs. These SAMs included octadecyltrichlorosilane (ODTS), octyltrichlorosilane (OTS), fluoroctyltrichlorosilane (FOTS), and hexamethyldisilazane (HMDS), representing a range of molecular sizes and chemical terminations ($-CH_3$ vs. $–CF_3$). In this work, we make use of x-ray intensity oscillations at the so-called anti-Bragg position to extract the occupation (coverage) of the individual layers as a function of time. These coverage-exposure relationships give us a direct measure of the (relative) probabilities of adsorption as a function of coverage. For the conditions examined (E_i = 5.1-12.3 eV, T_s = 40 °C) on all the starting surfaces (SiO_2 and SAM/SiO_2) we observe a decrease in the probability of adsorption with increasing incident energy indicative of trapping-mediated adsorption. The probability of adsorption on these starting surfaces is dependent on both the chain length and the chemical composition of the SAM, where the probability of adsorption is greatest on the thickest organic layer, ODTS, followed by OTS, SiO_2, FOTS, and HMDS. Once all surfaces are covered by DIP, however, the effects of incident kinetic energy are greatly reduced, and trapping is very efficient over the range of kinetic energies examined. For organic layers of comparable chemical composition and density, the initial probability of adsorption depends strongly on the layer thickness, where trapping on ODTS is most efficient, and on HMDS, least efficient. In a selected set of cases we will compare our experimental results with recent results from molecular dynamics simulations to obtain insight into the possible molecular-scale mechanisms/events that may occur in these systems. One such event appears to be the undeniable role of direct molecular insertion into the thicker organic layers such as ODTS.

9:20am **SS1-FrM4 Real-time Microscopic Investigations of the Growth of Thin Organic Films**, ***J.T. Sadowski***, Brookhaven National Laboratory, *A. Al-Mahboob, Y. Fujikawa, T. Sakurai*, Tohoku University, Japan

The growth mode, morphology, crystallinity and electronic structure of thin rubrene (5,6,11,12–tetraphenylnaphthacene: $C_{42}H_{28}$) films grown in ultra-high vacuum (UHV) conditions have been studied in situ in the low-energy electron microscope (LEEM).

Rubrene is attracting a considerable attention since it has shown promise in OTFT's, with field-effect mobilities of the single-crystal FET devices surpassing that of amorphous silicon and even pentacene. However, still little is known how the electronic and chemical properties of the substrate affect the crystallinity of rubrene thin films.

When rubrene is deposited on clean semiconductor surfaces, such as Si(111)-7x7, its reacts with the dangling bonds, partially dissociating and forming a disordered wetting layer. The nucleation of the crystalline islands follows, but high nucleation density and slow surface diffusion, due to a rough and disordered interface, result in a poor crystallinity of the films.

A completely different growth mechanism is observed upon rubrene deposition on semi-metallic Bi(0001) surface. In this case rubrene islands nucleate immediately, without formation of any wetting layer. Keeping the substrate temperature at 400K results in nucleation of large, single-crystalline rubrene islands preferentially oriented along the surface terraces. Low-energy electron diffraction (LEED) patterns indicate formation of a new rubrene phase. Most interestingly, this phase is characterized by chiral ordering of the molecules within single crystalline domains having sizes in the range of tenths of micrometers. Such chiral ordering has a great potential for improvement of the crystallinity of rubrene films, and thus performance of rubrene-based devices.

9:40am **SS1-FrM5 *In Situ* Characterization of Surfaces Following Soft and Reactive Landing of Complex Ions**, ***Q. Hu***, *P. Wang, P.L. Gassman, J. Laskin*, Pacific Northwest National Laboratory

Soft- and reactive landing (SL/RL) of mass-selected ions enables highly selective preparation of uniform thin films of a variety of complex molecules on surfaces. We have recently demonstrated covalent immobilization of several model peptides on the self-assembled monolayer (SAM) of N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM) using RL. Another remarkable finding is that SL and RL can be utilized for purification of peptide conformations that may not be stable in solution on SAM surfaces. For example, while Ac-Ala$_{15}$-Lys peptide mainly exist in its β-sheet conformation in solution, SL and RL of this peptide on the surface results in immobilization of a very stable α-helical conformation. This study presents a pathway for preparation of conformationally-selected peptide arrays that cannot be prepared using traditional solution-phase approaches. Here we present SL of singly and doubly protonated peptides (Gramicidin S, Substance P, Ac-Ala$_{15}$-LysH$^+$ and Ac-LysH$^+$-Ala$_{15}$) onto inert SAMs of alkylthiol (HSAM) and fluorinated alkylthiol (FSAM) on gold, and RL of singly protonated diamines and multiply protonated dendrimers onto reactive NHS-SAM and COF-terminated SAM surfaces. The modified SAM surfaces were characterized using *in situ* real time infrared reflection absorption spectroscopy (IRRAS) and secondary ion mass spectrometry (SIMS). *In situ* analysis of substrates during and after the SL/RL processes is essential for understanding charge transfer phenomena, reactivity of soft-landed molecules, and modification of the secondary structure of the molecule as a result of interaction with the surface.

10:00am **SS1-FrM6 Surface Deposition and Characterization of Cu Clusters Utilizing Soft-Landing Drift Tube Spectrometry**

G.F. Verbeck, *S. Davila*, University of North Texas

Intro

The soft-landing of ion cluster onto a surface is a novel approach for the deposition of specifically selected cluster. Our approach differs from current deposition/ soft landing techniques in that it allows specific molecule to be landed with a KE of around 1-5 eV where current soft-landing techniques are in the range around 30 - 50 eV. Large KE may not be ideal for the landing of metal clusters as the energy is translated into motion along the surface resulting in aggregation along defects in the surface. We have recently developed soft-landing system using a drift tube, high pressure (1 – 100 torr), and a modified substrate to create a soft-landing around 1 - 5 eV. Surface modifications can isolate clusters and protect them from aggregation. This soft-landing method allows for the characterization of a specific soft landed metal cluster on the surface via AFM, Raman Spectroscopy, and Electrochemistry.

Method

Our soft-landing instrument allows for the direct ablation of metal samples via laser or atmospheric plasma. Laser ablation of a metal sample by a pulsed Nd:YAG laser for duration of 1-3 hrs acts as our source for ion clusters. The instrument is operated at a pressure between 1-13 torr, with a voltage between 10-500 ±V that is applied uniformly across the drift tube. Helium is used as a buffer gas and acts as a means to control cluster formation. The high pressure narrows the clusters KE from 40 eV to about 1 eV through collisions via the buffer gas. Clusters travelling within the drift tube are separated based on collisonal cross-section. A pulsed split ring assembly at the end of the drift tube isolates specifically selected clusters directly on an unprepared or modified surface. The sample surface is then removed for characterization.

Data

Drift Tube spectra collected at 8 torr shows a cluster range of n = 1-8 along with corresponding Cu$_n$O. Clusters that have been landed on the surface are characterized using AFM. Images show an aggregation of the clusters in a striation patterns along the surface. The bridging across a defect instead of deposition within has also been seen. This clustering, aggregation, and growth shows a soft-landing has been made on the surface keeping the Cu cations and clusters intact. Self assembly of specifically isolated cluster groups has also been shown to occur on the surface of mica. Other characterization methods and various clusters may be specifically selected and landed with time allowing further development.

Instrument operates at pressure/temperature closer to ambient conditions than currently available, allowing ions to be soft landed on various modified surfaces for isolation and characterization.

10:20am **SS1-FrM7 Plasma Induced Interfacial Reaction of Hafnium Nano Particle and SiO$_2$ Film for Direct HfSiON Growth**

T. Kitajima, *T. Nakano,* National Defense Academy, Japan*, T. Makabe*, Keio University, Japan

In the paper, we show the example of the non-thermal chemistry over the nano-metal/semiconductor interface caused by the non-equiliblium low pressure RF plasma exposure. The process is directed to the new fablication scheme of high-k dielectric thin film for MOSFETs with fewer process steps, lower impurity, and minimised EOT (equivalent oxide thickness). In the process, high density hafnium metal nano particle with 4 nm diameter is formed on SiO2/Si surface and subsequent nitrogen plasma exposure (~10 min.) leads to the growth of HfSiON high-k dielectric film with SiN interfacial layer.

Current ULSI technology requires the use of hafnium related high-k dielectrics with ~3 nm thick for MOSFET to lower the power consumption. HfSiON is the most applicable chemistry for the high-k material with proper energy band alignment, large area uniformity, and thermal stability. The direct formation of HfSiO film from the Hf overlayer and underlying SiO2 utilizing the thermal interfacial reaction was previously proposed [1]. The process demonstrates remarkably low inpurity in the film due to the lack of carbon in contrast to the case of MOCVD processes. In our case, 2.5 nm thick Hf metal layer is deposited with e-beam deposition source on SiO2/Si(100) surface uniformly. The morphology obtained with the in-situ non-contact AFM measurement revealed the surface consists of the high density array of Hf nano particles with the size of 4 nm in diameter. The exposure of atomic nitrogen and ions from the non-equiliblium plasma enables the introduction of N into the film and increases the interfacial reaction rate of Hf and SiO. Within the first 1 min., the Hf nano particles are oxynitrided with the N atoms from the plasma and the O atoms supplied from the lower interface judging from the XPS analysis. The following plasma exposure (~10min.) enables the diffusion of Si atoms into the higk-k film from the underlying SiO layer. The Si content in the film increases with the exposure time and becomes comparable to the Hf content with 35 min. exposure. The XPS spectrum shows the Si incorporated is mostly nitrided in the film. The spectrum also indicates the interfacial SiO layer is nitrided and this leads to the minimized EOT of the high-k stack structure.

[1] H. Watanabe, Appl. Phys. Lett. 85, 449 (2004).

10:40am **SS1-FrM8 Modeling Thin Film Deposition Processes in an HDP-CVD Reactor**

A. Bhoj, *K. Shah,* ESI US R&D, Inc.*, M. Megahed,* ESI Group, Inc.*, P. Kothnur, R. Kinder*, Novellus Systems, Inc.

Modeling HDP-CVD processes for high quality dielectric film deposition in high aspect ratio device structures remains a challenging task. A number of details such as the reactor geometry, inductive and capacitive power deposition, gas-phase chemistry and surface kinetics need to be addressed in a coupled manner. In this multi-physics approach, a reactor scale model in conjunction with a feature scale model is used to investigate the process dependence of deposition rates across the wafer and within features. Plasma properties, gas flow and deposition at the walls are addressed in the reactor scale model. The resulting film growth inside microscopic trenches is captured in the feature scale model. The reactor geometry is similar to that described in an earlier publication [1]. Data for gas phase and surface reaction kinetics are obtained from published literature [2]. In an earlier work [3], trends in deposition rate at the wafer with inductive power were discussed. In this paper, the impact of reactor scale process parameters such as bias power deposition, gas flow rates and wafer temperature on deposition at the wafer are investigated, and modeling results are compared to experimental data [4].

[1] M. Tuszewski and J. A. Tobin, *J. Vac. Sci. Technol. A* **14**, 1096 (1996).

[2] E. Meeks, *et al*, *J. Vac. Sci. Technol.* **A 16**, 544 (1998).

[3] A. Bhoj, *et al*, *EuroCVD and CVD XVII, 216th Meeting of the Electrochemical Society*, Vienna, Austria (2009).

[4] A. Bhoj, P. Kothnur, and R. Kinder, *61st Annual Gaseous Electronics Conference*, Dallas, TX (2008).

11:00am **SS1-FrM9 Ion Scattering Studies of Isolated Au Nanoclusters**

S. Balaz, J.A. Yarmoff, ***R.D. Gann***, University of California, Riverside

Isolated Au nanoclusters are grown atop amorphous solid water (ASW) at low temperature. This process, which represents the first step in the growth of nanoclusters via the buffer layer assisted growth (BLAG) method, is a unique way in which to fabricate small deposited clusters that have minimal interactions with a substrate. Such clusters are able to serve as model systems for investigations of how nanocluster electronic structure depends on shape and size. Low energy alkali ion scattering was used to probe the atomic and electronic structures of the clusters *in situ*. ASW was first deposited as a separation layer onto SiO$_2$/Si(111) at liquid nitrogen temperature, and then Au was evaporated onto the ASW to form nanoclusters. The mean size of the clusters is expected to increase with increased Au deposition. Time-of-flight (TOF) spectroscopy was used to collect charge-resolved spectra of scattered 2 keV $^7Li^+$ and $^{39}K^+$ ions. Spectra collected following small Au depositions display only a sharp single scattering peak, while multiple and plural scattering features are present following larger depositions. The change in spectral shape is indicative of the formation of multilayer nanoclusters. The experimental findings are interpreted with the aid of Monte-Carlo ion scattering simulations. 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. The lack of any angular dependence to the neutralization implies that the clusters behave as atomic-like structures. Further experiments will investigate how the clusters evolve when deposited onto the substrate by heating to desorb the ASW layer.

11:20am **SS1-FrM10 Initial Nucleation and Growth of Oxide Scale on Haynes® 214®Alloy**, ***V. Shutthanandan***, *S.V.N.T. Kuchibhatla, A.S. Lea, Z. Zhu, M.H. Engelhard, S. Thevuthasan,* Pacific Northwest National Laboratory, *P. Singh,* University of Connecticut, *V. Deodeshmukh,* Haynes International, Inc., *H. GhezelAyagh*, Fuel Cell Energy, Inc.

A combination of ion beam and electron spectroscopy techniques have been used to precisely understand the initial oxidation of a multicomponent alloy system, Haynes®214®. Surface sensitive nature of these techniques has been rightly exploited to precisely identify different phases formed at different times of oxidation. Haynes® 214® is a high temperature, Ni-Cr-Al-Fe based alloy, widely used in a plethora of applications ranging from “clean firing” of ceramics to the gas turbine industry. Various reports exist in the literature, which describe the long term stability of this alloy under oxidizing environments at temperatures above 900^{o}C. *Despite the number of applications and significant interest in this alloy, a clear mechanism of the early stage oxidation has not been documented.* An effort is underway to estimate the initial nucleation and growth of oxide scale on this alloy in various environments (such as dry and humid air). A combination of ion and electron based techniques such as Rutherford backscattering spectrometry (RBS), nuclear reaction analysis (NRA), particle induced x-ray emission (PIXE), secondary ion mass spectrometry (SIMS) and Auger electron spectroscopy (AES) and x-ray photoelectron spectroscopy (XPS) were used to measure the initial nucleation of the oxide scale on this alloy. NRA was used to track the oxygen depth profile while PIXE and RBS were used to track the changes in matrix components of the alloy for the formation of oxide scale for as-low-as 1 min of oxidation. Chemical analysis of this early stage of oxidation formation was studied by AES and XPS. Chemical surface mapping obtained from Auger analysis indicated that the initial oxide formed is chromia which is completely dominated by alumina after 7 min of oxidation treatment at 900^{o}C in air. Various merits of this work will be discussed along with possible future scope for using Ion beam techniques for processes such as oxidation of metals, a most widely studied problem.

Surface Science
Room: N - Session SS2-FrM

Semiconductor Surfaces and Interfaces II: Si
Moderator: C.L. Hinkle, University of Texas at Dallas

8:20am **SS2-FrM1 Observation of Realtime Oxidation of Si(111) Surfaces using Second Harmonic Generation**, ***K. Gundogdu***, *B. Gokce, E.J. Adles, D.E. Aspnes*, North Carolina State University

Realtime material diagnostics during material growth is commonly used in industrial applications. Linear optical methods specifically spectroscopic ellipsometry (SE) probe thin film thickness with a nanometer precision by measuring the change in dielectric susceptibility during material growth. However SE is a spatially averaging technique and therefore can not probe the chemical change at the bond level. In this work we show that second harmonic generation experiments can be used to directly visualize changes in interface and surface bonds in realtime, providing a powerful bond structure characterization tool. We employed SHG experiments to probe the oxidation of hydrogen terminated Si(111) surfaces. We are able to extract the oxidation rates for different bonds on Si(111) surfaces that are nominally flat and with vicinal cut. We found that the initial hydrogen termination process effects the oxidation rate in the bond level. We compare the results of SHG measurements with that of spectroscopic ellipsometry.

8:40am **SS2-FrM2 Surface Passivation Mechanism of Atomic Layer Deposited Al_2O_3 Films on *c*-Si Studied by Optical Second-Harmonic Generation**, ***N.M. Terlinden***, *J.J.H. Gielis, V. Verlaan, G. Dingemans, M.C.M. van de Sanden, W.M.M. Kessels*, Eindhoven University of Technology, Netherlands

Recently, it was shown that Al_2O_3 thin films synthesized by (plasma-assisted) atomic layer deposition (ALD) provide excellent surface passivation of *n, p* and p^+ type *c*-Si as highly relevant for *c*-Si photovoltaics. It was found that a large *negative* fixed charge density (up to 10^{13} cm^{-2}) in the Al_2O_3 film plays a key role in the passivation mechanism of Al_2O_3 [1, 2]. The surface passivation quality of Al_2O_3 strongly increases with film thickness before reaching saturation around 10 nm as determined by carrier lifetime spectroscopy. In this contribution a study into the thickness effect will be presented in order to distinguish between the influence of field-effect passivation, *i.e.* electrostatic shielding of charge carriers by the fixed negative charge, and chemical passivation, *i.e.* by a reduction of the interface defect density. To this goal the nonlinear optical technique of second-harmonic generation (SHG) has been utilized. SHG is highly surface and interface specific and allows for the contactless determination of internal electric fields ($\geq 10^5$ V/cm^{-1}). Spectroscopic SHG, carried out with a femtosecond Ti:sapphire laser tunable in the 1.33-1.75 eV photon energy range, has revealed a thickness independent electric field for Al_2O_3 films with thicknesses ranging from 2 to 20 nm. This implies that the field-effect passivation is not affected by the film thickness and that the thickness dependence in passivation quality can be attributed to a changing level of chemical passivation. Moreover, this result confirms that the fixed negative charges are located at the Al_2O_3 interface as also indicated by conventional C-V measurements. In addition, SHG shows clear differences between measurements performed on Al_2O_3 films grown by thermal and plasma-assisted ALD. These are likely related to the properties of the interfacial SiO_x induced by either growth process. The presence of this oxide is suggested to be responsible for the chemical passivation quality. Furthermore, the differences indicate a smaller contribution of field-effect passivation for the Al_2O_3 grown with thermal ALD compared to the film from the plasma-assisted process. These results have led to a deeper understanding of the c-Si surface passivation by Al_2O_3 as will be discussed.

[1] B. Hoex *et al.* J. Appl. Phys. **104**, 044903 (2008)

[2] J.J.H. Gielis *et al.* J. Appl. Phys. **104**, 073701 (2008)

9:00am **SS2-FrM3 Influence of Alkali-Metal Adsorption on Phase Transition of In/Si(111)-4 × 1 Surface**, ***H. Shim***, *W. Lee, G. Lee,* Inha University, Republic of Korea, *S. Yu, J. Koo*, Korea Research Institute of Standards and Science

One monolayer of In on a Si(111) surface forms 4×1 structure at room temperature (RT). This In/Si(111)-4×1 surface has a quasi- one dimensional (1D) metallic electronic structure and undergoes a symmetry-lowering phase transition into an insulating 8×2 phase at low temperature (LT) upon cooling the sample below approximately 130 K [1]. Adsorption of Na atoms on the surface was reported to convert the 4x1-RT phase into the 8×2-LT phase even at RT [2]. We investigated using low-energy electron diffraction (LEED) the influence of alkali-metals (Na, K, Li) adsorption on the structural phase transition of this quasi-1D In/Si(111) surface. Introducing the alkali metals with low coverage on the surface at room temperature was found to affect the 4×1-to-8×2 structural phase transition by lowering the transition temperature (Tc). The Tc decreased almost linearly and the transition becomes more rounded when the amount of deposited alkali-metals atoms was increased. The decrease of Tc with the increase of the amount of adsorbed Na atoms is suggested to be due to the doping of electrons from adsorbates to the substrate [3]. In the high-coverage regime, new superstructures appear in LEED with the adsorption of alkali metals. Comparison of the adsorbate-induced superstructures in low-coverage and high-coverage regimes will be made and discussed.

[1] H. W. Yeom, et al., Phys. Rev. Lett. 82, 4898 (1999)

[2] S. S. Lee, et al., Phys. Rev. Lett. 88, 196401 (2002)

[3] H. Shim, et al., Appl. Rev. Lett. *in press* (2009)

9:20am **SS2-FrM4 The First Attachment of Polybutadiene and Functionalized Polybutadiene to Hydrogen-Terminated Silicon, with Post-Derivitization of these Adsorbed Species**, *E. Nelsen, T. Wickard,* Brigham Young University, *H. Schlaad,* Max Planck Institute of Colloids and Interfaces, Germany, *R.C. Davis,* ***M.R. Linford***, Brigham Young University

We report the first attachment of polymers with pendant vinyl groups to hydrogen-terminated silicon(111) (Si(111)-H) under mild conditions; 1,2-addition polybutadiene (Mw 3200-3500) in solution was attached to Si(111)-H at room temperature with only visible light activation. We also report the partial functionalization, in solution, of 1,2-addition polybutadiene with various thiols using thiol-click chemistry and the subsequent attachments of these compounds to Si(111)-H. The partially functionalized polybutadienes allow further functionalization at the surface through their unreacted carbon-carbon double bonds, as demonstrated with a perfluorinated thiol. We present this as a useful strategy for silicon surface modification. Surfaces were characterized with contact angle goniometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM).

9:40am **SS2-FrM5 Mechanistic Study of Photochemical Grafting of Alkenes to Group IV Semiconductors**, ***X. Wang***, *J. Streifer, P. Colavita, R.J. Hamers*, University of Wisconsin-Madison

The grafting of organic molecules on semiconductor surfaces initiated by UV light has become an efficient means to tailor the chemical and physical properties of surfaces of materials, enabling their integration with various applications of the devices. *In situ* photoelectron yield experiments were performed in the spectral range from 3 to 6 eV on alkene liquid/nanocrystalline diamond (NCD) interfaces. *N*-Alkenes carrying different terminal functional groups: trifluoroacetamide-protected 1-aminodec-1-ene (TFAAD) and 10-N-Boc-aminodec-1-ene (tBoc) were used to investigate the dependence of photoelectron yield on the energy of the molecular acceptor level. Amorphous carbon was used in addition to NCD to study the influence of the substrate electronic structure on the photoelectron yield threshold. The photochemical attachment of TFAAD on H-terminated NCD surfaces at various incident photon energies was characterized by X-ray photoelectron spectroscopy (XPS) to investigate the correlation between the excitation energy and the reaction efficiency. These measurements reveal that the photochemical reaction on carbon surfaces is initiated via the photoejection of electrons from the solid valence band into the acceptor levels of the alkenes. SEM images of patterned molecular layers on two H-terminated single crystal diamonds (SCD, type Ib and IIb) with different hole mobilities reveal much sharper transition between functionalized and non-functionalized regions on the sample with much lower hole mobility (type Ib SCD). However, the surface coverage of grafted alkenes as characterized by XPS is quite similar on these two surfaces. These data imply that while the photoemission of electrons controls the reaction efficiency, the holes left in the substrates can diffuse and control the grafting sites.

Recent data exploring the mechanism on silicon will also be presented. Our comparison of silicon and diamond suggests that there are some common factors underlying the ability to graft alkenes onto various semiconductors, but also some important differences. These results suggest that photochemical grafting may be broadly applicable to a wide range of materials, and that a fundamental understanding of the mechanism facilitates the design and synthesis of well defined functional interfaces.

10:00am **SS2-FrM6 Structure and Order of Organophosphonate Self-Assembled Monolayers on Si(100)**, ***M. Dubey***, *T. Weidner, L.J. Gamble, D. Ratner, D.G. Castner*, University of Washington

Organophosphonic acid self-assembled monolayers on oxide surfaces have seen growing use in electrical and biological sensor applications [1-2]. Molecular order in organophosphonic acid SAMs is highly desirable for reproducible electronic properties of these modified surfaces. In this regard, packing and order of the SAMs is important, as it influences the electron transport measurements. In this study, we examined the order of the phosphonate films deposited on silicon oxide surface by the Tethering By Aggregation and Growth (T-BAG) method [3] using various state-of-art surface characterization tools. Near edge x-ray absorption fine structure (NEXAFS) spectroscopy is used to study the order of a methyl- and hydroxyl- terminated phosphonate SAMs in vacuum and sum frequency generation (SFG) spectroscopy is used to study their order in aqueous condition. X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) on these samples confirm the presence of chemically intact monolayer phosphonate films. NEXAFS spectroscopy confirmed a considerable degree of molecular order in the octadecylphosphonic acid (ODPA) and 11-hydroxyundecylphosphonic acid (PUL) films with a tilt angle of 37° and 47° respectively. *In situ* SFG studies in deuterated water were conducted to determine the order of these films under biologically relevant conditions. The ODPA film showed the peaks for terminal methyl units, which are expected for ordered films. PUL films also showed a considerable degree of alignment indicated by resonances of the methylene unit next to the terminal hydroxyl group. These studies indicate that well ordered SAMs with methyl or hydroxyl termination can be prepared on oxide surfaces using phosphonate headgroups. These surfaces can be subsequently used to anchor biomolecules for biomaterial and biosensor applications.

[1] A. Cattani-Scholz, D. Pedone, M. Dubey, S. Neppl, B. Nickel, P. Feulner, J. Schwartz, G. Abstreiter, M. Tornow, *Acs Nano* **2008**, *2*, 1653.

[2] H. Klauk, U. Zschieschang, J. Pflaum, M. Halik, *Nature* **2007**, *445*, 745.

[3] E. L. Hanson, J. Guo, N. Koch, J. Schwartz, S. L. Bernasek, *Journal of the American Chemical Society* **2005**, *127*, 10058

10:20am **SS2-FrM7 Hydrogen-bond Mediated Chemistry of Glycine on Si(111)7×7: A Catch-And-Release Approach to Surface Functionalization**, ***K.T. Leung***, University of Waterloo, Canada

The growth of glycine film by thermal evaporation on Si(111)7×7 at room temperature has been studied by X-ray photoelectron spectroscopy (XPS) and scanning tunneling microscopy (STM). In contrast to the common carboxylic acids, glycine is found to adsorb on the 7×7 surface through dissociation of the N-H bond (instead of the O-H bond). The presence of a transitional adlayer between the first adlayer and the zwitterionic multilayer is identified by its characteristic N 1s XPS features attributable to intermolecular N-to-HO hydrogen bond. An intramolecular proton transfer mechanism is proposed to account for the adsorption process through the amino group. We also demonstrate that the observed transitional adlayer can be used as a flexible platform to “catch-and-release” biomolecules with compatible H-bonding active sites in a controllable and reversible manner. Intricate evolution of the surface adsorption arrangement during the initial growth has also been monitored by STM. Early evidence of collective assembly of glycine into novel structures in the nanometer length scale could be found.

10:40am **SS2-FrM8 Site-selective Reactivity of Ethylene on Si(001) induced by Local Electronic Distortions**, ***G. Mette***, *C.H. Schwalb*, Uni Marburg, Germany, *M. Dürr*, Hochschule Esslingen, Germany, *U. Höfer*, Uni Marburg, Germany

The adsorption of organic molecules on semiconductor surfaces is of special interest with respect to surface functionalisation and its use in molecular electronics. Due to the localized electronic states of a semiconductor surface, its reactivity strongly correlates with the local electronic properties of the dangling-bond states. Dissociative adsorption of H_2 on Si(001), e.g., shows pronounced site-selective reactivity at steps or preadsorbed atomic hydrogen [1].

In this study, we test the concept of site-selective reactivity at locally distorted configurations for more complex, organic molecules. On that account, the adsorption of ethylene on clean and hydrogen precovered Si(001) surfaces has been investigated by means of scanning tunneling microscopy. On the clean surface, two ethylene adsorption geometries were identified with ethylene adsorbed on one and two dimers, respectively. The latter adsorption geometry shows significantly lower reactivity and has not been observed so far. Preadsorption of atomic hydrogen and the concomitant distortion of the electronic states is found to increase the reactivity of this two-dimer adsorption pathway by almost two orders of magnitude. Its site selective reactivity thus surpasses that of the one dimer configuration on the clean surface.

The results are rationalized in the framework of a precursor mediated adsorption process. Our experiments indicate that the conversion barrier between precursor and final chemisorbed state can be efficiently controlled by changing the local electronic structure of the surface. Thus, locally distorted dangling-bond configurations allow for the control of site-selective reactivity also in the case of barrierless, non-dissociative adsorption of an organic molecule.

[1] M. Dürr and U. Höfer, Surf. Sci. Rep. 61, 465 (2006)

11:00am **SS2-FrM9 Identifying Adsorbate Structures on Semiconductor Surfaces Using Simulated Scanning Tunneling Microscope Images**, *L. Yang*, ***D. Doren***, University of Delaware

Simulated Scanning Tunneling Microscopy images, based on first-principles calculations, have been used to characterize adsorption products of organic molecules on semiconductor surfaces and assign molecular structures to specific features in experimental STM images. Three examples are presented: 1) Styrene molecular lines on the H-terminated Si(100)-2x1 surface system exhibit several novel molecular conductance phenomena. First-principles calculations show that the phenyl ring orientation at chain ends are fluxional, favoring structures with the terminal ring arranged perpendicular to the molecular line. Simulated STM images show that the tunneling current depends strongly on the phenyl ring orientation, since it controls the coupling between the charged dangling bond and the styrene π system. The perpendicular orientation shows higher conductivity than the parallel one, increasing the apparent height of the molecule at the end of the row. This is consistent with experimental observations, while the simulated images of the parallel-ring geometry are not. Because such subtle changes in molecular structure control the flow of electrical currents, STM can be used to distinguish these conformations. 2) The bonding configuration of styrene attached to the bare Si(111)-7x7 surface is not known from spectroscopic measurements, though two likely possibilities have been identified. Matching simulated empty-state and filled-state STM images to new experimental observations provides strong evidence that the attachment of styrene to Si(111)-7x7 is by a [4+2] cycloaddition, involving both the external $-CH=CH_2$ and a C=C inside the phenyl ring. A comparison experimental images to theoretical predictions of the bias dependence for the two binding structures is critical to this identification. 3) Three unsaturated organic molecules – styrene, phenyl acetylene, and benzaldehyde – were attached to the H-terminated Si(111) surface through analogous radical chain reactions. Both simulated and experimental STM images of the three molecules show significant differences in apparent height, despite small differences in physical height. Thus STM is sensitive to the functional group used to link the molecule to the surface. The simulations also suggest a new scanning protocol that can enhance the contrast among molecules. The so-called "local constant height" STM images, which probe the spatial variation of conductance, show distinctive features for the three molecules that can be used to tell the molecules apart very easily.

11:20am **SS2-FrM10 Defect Engineering via Modification of Semiconductor-Oxide Interfaces**, ***P. Gorai***, *Y. Kondratenko, E.G. Seebauer*, University of Illinois at Urbana-Champaign

The behavior of defects within silicon can be changed significantly by controlling the chemical state at nearby surfaces or solid interfaces. Experiments have shown that certain chemical treatments change the ability of a free surface to act as a "sink" for point defects such as interstitials. When the surface is made chemically active, this ability rises. The surface can then remove Si interstitials selectively over impurity interstitials and such behavior can be kinetically quantified through an annihilation probability. Although annihilation probabilities for interstitials have been measured under various conditions for free surfaces, very little understanding exists for the corresponding quantity at solid-solid interfaces. Understanding of interface influence on interstitial annihilation is very important in fabrication of advanced transistors for post-implantation damage removal and dopant activation. The present work seeks to develop scientific understanding of interface activity for Si interstitial annihilation and measure the annihilation probabilities at interfaces between silicon and several kinds of oxides and nitrides. Diffusion of isotopically labeled Si (mass 30) in Si host lattice was used as a marker for elucidating how changes in the $Si-SiO_2$ interface affected Si self-diffusion after annealing. Marked differences are observed among the various interfaces. Continuum simulations of the measured SIMS profiles were subsequently employed to quantify annihilation rates at the $Si-SiO_2$ interface.

Thin Film
Room: B4 - Session TF-FrM

Transparent Electronic Materials and Applications
Moderator: M. Creatore, Eindhoven University of Technology, The Netherlands

8:20am **TF-FrM1 Thin-film Barrier on Foil for Roll-to-Roll OLEDs**, ***F.J.H. van Assche***, *E.W.A. Young, J.J. Michels,* TNO Holst Centre, The Netherlands, *G.H. Rietjens, P. van de Weijer, P.C.P. Bouten,* Philips Research Laboratories, The Netherlands, *A.M.B. van Mol*, TNO Holst Centre, The Netherlands

A flexible multi-layer ultra-barrier stack consisting of stacked silicon nitride layers interleaved by planarization layers has been developed for encapsulation of OLEDs on foil.

For this purpose a low temperature (<120°C) silicon nitride, deposited using a RF-driven parallel plate plasma reactor, has been optimized both on c-Si and on PEN foil by using spectroscopic ellipsometry (SE) and Fourier transform infrared spectroscopy (FTIR).

However, while intrinsically very low water vapour transmission rates (WVTR $<<10^{-5}$ $g/m_2/day$ at room conditions) of the SiN can be achieved, the total flux of water through the barrier stack is eventually determined by the presence of local defects or pinholes. To gain insight in the transport mechanism of water in the barrier stack, both modelling and a method to trace pinholes in the barrier stack has been applied. On samples (both Ca-mirrors and OLEDs) excellent correspondence of local decay to local presence of water in the barrier stack has been shown.

Ca mirror tests of these barriers on PEN foil have yielded spotless devices after several weeks of accelerated lifetime testing at 60°C and 90% RH and even at 85°C/85% climates. Accelerated lifetime testing at 60°/90% of encapsulated OLEDs resulted in a significant yield of 6 cm^2 OLED devices without visible black spots due to cathode oxidation for over 3 weeks in this harsh climate.

Mechanical compatibility of the barrier coating with respect to R2R processing has been verified by means of bending tests of SiN layers on foil. As a next step towards R2R processing of barriers, the feasibility of R2R compatible plasma deposition by means of in-line microwave driven plasma sources is investigated. Barrier layer quality is monitored as a function of deposition rate and thickness.

8:40am **TF-FrM2 Study on MoO_{3-x} Films Deposited by Reactive Sputtering for Organic Light-Emitting Diodes**, ***N. Oka***, *H. Watanabe, Y. Sato,* Aoyama Gakuin University, Japan, *N. Ito, H. Tsuji,* Panasonic Electric Works Co., Ltd., Japan, *Y. Shigesato*, Aoyama Gakuin University, Japan

Molybdenum trioxide (MoO_3) films have been expected as a material that accelerates the hole-injection from the anode to the organic layer in organic light-emitting diodes (OLEDs) [1], where the hole-injection mechanisms into the organic layer have been discussed actively. It has been reported that the hole-injection performance of MoO_3 films would be dependent on stoichiometry of the MoO_{3-x} [2] and forming a charge-transfer complex between the MoO_3 layer and the hole-transport layer (HTL) for OLEDs [3,4]. In this study, MoO_{3-x} ($x \leq 1$) films were deposited by radio frequency (rf) magnetron sputtering using a Mo metal target at a power of 200 W. Total gas pressure of the mixture of argon (Ar) and oxygen (O_2) was maintained at 1.0 Pa. The O_2 gas flow ratio (f_{O2}) [$O_2/(Ar+O_2)$] during the sputtering process was varied 0-100%. The electronic state of the MoO_{3-x} films near the surface was analyzed by X-ray photoelectron spectroscopy (XPS) and photoelectron spectrometry in air (PESA). The chemical shift of the XPS Mo3d peak revealed that the valence electron numbers of Mo were four or six for the film deposited at 10 % f_{O2}, whereas it was approximately six for the films deposited at f_{O2} of higher than 15%. Furthermore, the PESA characteristics indicated that localized defect levels, caused by oxygen defects in MoO_{3-x}, should be generated between the Fermi level and the valence band, the amount of which varied with f_{O2}. These results suggest that the amount of oxygen in the films was controllable by appropriate adjustment of f_{O2}. In order to evaluate the chemical reaction between each MoO_{3-x} layer and HTL by Raman spectroscopy, bilayer films was fabricated by subsequent vacuum evaporation of N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (α-NPD) as HTL. The Raman spectra indicate that a charge transfer complex should be generated at an interface of the bilayers and the amount varied slightly with f_{O2}, which could be expected to promote hole-injection and thereby enhance the device performance of OLEDs.

<Acknowledgment>

This work was supported by New Energy and Industrial Technology Development Organization (NEDO) as a project of "Development of High-efficiency Lighting Based on the Organic Light-emitting Mechanism".

[1] T. Matsushima, G-H. Jin, H. Murata, J. Appl. Phys. 104, 054501 (2008).

[2] K. Sakanoue, Device Physics, Material Chemistry, and Device Application of Organic Light Emitting Diodes, CMC Publishing, 129 (2008) (in Japanese).

[3] W.-J. Shin, J.-Y. Lee, J. C. Kim, T.-H. Yoon, T.-S. Kim, O.-K. Song, Organic Electronics 9, 333 (2008).

[4] G. Xie, Y. Meng, F. Wu, C. Tao, D. Zhang, M. Liu, Q. Xue, W. Chen, Y. Zhao, Appl. Phys. Lett. 92, 093305 (2008).

9:00am **TF-FrM3 Amorphous and Crystalline Metaloxide Semiconductors for Transistor Applications**, ***A. Facchetti***, Northwestern University **INVITED**

In this presentation I will discuss our latest results in developing semiconductor metal oxide (SMO) formulations for solution-processed thin-film transistors based on crystalline and amorphous metal metaloxide films. Solution-processed amorphous semiconductor film fabrication by spin-coating and eventually printing is advantageous because of process simplicity, low cost, high reproducibility, chemical composition/stechiometry control, and possible high throughput enabling inexpensive electronics. Regarding crystalline SMO films, In_2O_3 thin-film transistors (TFTs) were fabricated on various dielectrics [SiO_2 and self-assembled nanodielectrics (SANDs)] by spin-coating In_2O_3 film precursor solutions consisting of methoxyethanol (solvent), ethanolamine (EAA, base), and $InCl_3$ as the In^{3+} source. Importantly, an optimized film microstructure characterized by the high-mobility In_2O_3 004 phase, is obtained only within a well-defined base: In^{3+} molar ratio after annealing at 400 C. The greatest electron mobilities of ~ 44 cm^2, for EAA :In^{3+} molar ratio = 10, $V^{-1}s^{-1}$, is measured for $n^+-Si/SAND/In_2O_3/Au$ devices. This result combined with the high $I_{on}:I_{off}$ ratios of ~ 10^6 and very low operating voltages (< 5 V) is encouraging for high-speed applications. We have also developed amorphous Sn-In-O and Zn-Ga-In-O formulations in which the corresponding films can be annealed at far lower temperatures (< 250 ºC). For instance, solution-processed amorphous tin-doped indium oxide (ITO) films for TFT fabrication at temperatures <250 °C can be achieved by controlling film precursor solution In $^{+3}$ vs. Sn $^{+4}$ molar ratio resulting in electron mobilities > 2 $cm^2 V^{-1}s^{-1}$ and $I_{on}:I_{off} > 10^4$ for TFTs using SiO_2 as the gate dielectric. Furthermore, we demonstrate that hybrid integration of solution-processed ITO semiconductor films SAND enables m ~ 20 $cm^2 V^{-1}s^{-1}$.

9:40am **TF-FrM5 Permittivity-Engineered TCOs Studied by *In Situ* Spectroscopic Ellipsometry*, J. Burst*,** National Renewable Energy Laboratory*, T.J. Peshek,* Arizona State University and National Renewable Energy Laboratory*, X. Li, T.A. Gessert, D.H. Levi,* National Renewable Energy Laboratory*, B.R. Rogers, S. Weiss*, Vanderbilt University

Recently, Gessert *et al* have reported on improved infrared optical transmittance of indium oxide-based transparent conductive oxides (TCOs) by addition of zirconia [1]. Their results show that zirconia addition allows for deposition conditions with a wider range of oxygen partial pressures while maintaining suitable optical performance. Here we report on our real-time spectroscopic ellipsometry (SE) sputter deposition studies of permittivity-engineered TCOs. *In situ* ellipsometry gives information on the growth dynamics and optical functions during film deposition. We map out the phase space of this system with regard to temperature, partial pressure of oxygen and zirconia content. Temperature-dependent Hall measurements indicate a critical point at which the films are non-degenerate. We further correlate the optical and electrical data with structural and compositional analysis.

[1] T.A. Gessert, Y. Yoshida, C.C. Fesemaier, and T.J. Coutts, *J. Appl. Phys.*, **105** (2009).

10:20am **TF-FrM7 Reactive Magnetron Sputter Deposition of Al-doped ZnO Films with Unipolar Pulsing and Impedance Control System*, Y. Nishi*,** *K. Hirohata, N. Tsukamoto, Y. Sato, N. Oka, Y. Shigesato*, Aoyama Gakuin University, Japan

Transparent conductive oxide (TCO) is a highly degenerated wide band-gap semiconductor with low electrical resistivity and high transparency in the visible and near-infrared regions. Al-doped ZnO (AZO) should be promising potential alternative to In-based TCO, such as ITO or IZO. AZO films have been prepared by magnetron sputtering using ceramic targets because of the various advantages for uniform depositions in large area. In general the deposition rate for the sputtering using the oxide ceramic targets is not so high and also the cost for the high quality ceramic targets is high. On the other hand, reactive sputtering using Zn-Al alloy targets is considered to be one of the most promising techniques to achieve much higher deposition rate for various industrial applications because sputtering yield of the metallic surface is much larger than oxide surface and also the higher sputtering power density can be applied for metallic targets because of their higher thermal conductivity. The reactive sputtering process, however, is strongly affected by the O_2 flow ratio; the deposition rate exhibits hysteresis with respect to the O_2 reactive gas flow rate. Such behavior originates in the oxidation state of the target surface, resulting in the marked decrease in deposition rate with the increasing O_2 flow. Therefore, the sputtering conditions should be precisely controlled so as to obtain high-quality AZO films by reactive sputtering with a high deposition rate and with high reproducibility. In this study, AZO films were deposited on quartz glass substrates, unheated and heated at 200°C, using reactive sputtering with a specially designed feedback system (Fraunhofer Institut fur Elektronenstrahl-und Plasmatechnik, FEP) of discharge impedance combined with mid-frequency (mf) pulsing [1] . A planar Zn-Al alloy target (Al: 1.5wt.%) was connected to the switching unit, which was operated in a 50 kHz unipolar pulse mode [2] . Oxidation of the target surface was precisely controlled by the feedback system control the entire O_2 flow ratio in the "transition region". The deposition rate was about 10-20 times higher than the one deposited by conventional sputtering depositions using oxide ceramic targets. For the AZO films deposited on the glass substrates heated at 200°C with a discharge power of 4000 W, the deposition rate was 390 nm/min, where the resistivity of the films was 3.8×10^{-4} Ωcm and transmittance in the visible region was 85 %.

[1] M. Kon, P.K. Song, Y. Shigesato, P. Frach, A. Mizukami and K. Suzuki, Jpn. J. Appl. Phys. 41, 814 (2002).

[2] S. Ohno, N. Takasawa, Y. Sato, M. Yoshikawa, K. Suzuki, P. Frach and Y. Shigesato, Thin Solid Films 496, 126 (2006).

10:40am **TF-FrM8 Study on Spatial Distribution of Electrical Properties for Al-doped ZnO Films Deposited by DC Magnetron Sputtering using Various Inert Gases*, Y. Sato*,** *K. Ishihara, N. Oka, Y. Shigesato*, Aoyama Gakuin University, Japan

Due to recent shortages [1] and toxicity issues [2] of indium, Al-doped ZnO (AZO) have attracted much attention as alternatives to transparent conductive materials, such as Sn-doped In_2O_3 (ITO) films and indium zinc oxide (IZO). In general, AZO films deposited by magnetron sputtering showed large spatial distributions of electrical properties. Several investigations have suggested that such electrical property distributions should originate in the bombardments of the high-energy negative oxygen ions accelerated in cathode sheath region [3] or the oxidation enhancement by the activated oxygen sputtered from the oxide target and reaching at the growing film surface [4], both of which should take place at the locations in front of the erosion area of the magnetron cathode. In order to clarify the mechanisms of the degradation in the electrical properties, we investigated the dominant factors determining the electrical property distributions of AZO films deposited by dc magnetron sputtering using various sputtering gases, such as Ar, Kr or Xe. The spatial distributions clearly showed the dependence on a variety of the sputtering gases when the films were deposited on unheated glass substrate. In the cases of using Kr or Xe gases, the tendency to increase in the resistivity at the location in front of the erosion area was enhanced extremely compared with the case of using Ar. This could be attributed to the bombardment damages enhanced by the increasing sputtering voltages, because the plasma impedance increased by the smaller secondary electron emission coefficients for Kr or Xe impingements. We will also discuss on the oxidation effect of the activated oxygen or the bombardment effects by the high energy neutrals (Ar, Kr or Xe) on the electrical property distribution of AZO films. This work was partially supported by a High-Tech Research Center project for private universities with a matching fund subsidy from the Ministry of Education, Culture, Sports, Science, and Technology (MEXIT) of Japan.

[1] III-Vs Review 18 (8) (2005) p12.

[2] T. Homma et al., J. Occup . Health, 45 (2003) 137; T. Hamaguchi et al., Occup. Environ. Med. 65 (2008) 51.

[3] K. Tominaga et al., Jpn. J. Appl. Phys. **27**, 1176 (1988).

[4] T. Minami et al., J. Vac. Sci. Technol. A **18**, 1584 (2000)

11:00am **TF-FrM9 Multilayer Active Coatings on Flexible Polymer Sheet using High Rate, Closed Field Reactive Sputtering*, J.M. Walls*,** Loughborough University, UK*, D.R. Gibson, S. Stanley, A.R. Waugh*, Applied Multilayers Ltd, UK

There is an increasing requirement for depositing complex multilayer active coatings on to surfaces of flexible polymer sheet. Applications include thin film photovoltaics, electrochromic coatings and displays. Coating materials include transmitting conducting oxides such as ITO, dielectric metal-oxides, refractory metal-oxides and metal conductors. Coating flexible polymer sheet presents a challenge since it requires a low temperature process that deposits thin films that are spectrally stable but also low in stress to prevent cracking.

This paper describes a flexible reactive sputtering process in which adjacent unbalanced magnetrons are constructed of opposite magnetic polarity. The resulting closed magnetic field maintains a high density reactive plasma. In contrast to previous reactive sputtering strategies, the process does not require an auxiliary ion or plasma source and the associated use of high Voltage ion acceleration. As a result, the deposition energy is optimized and insufficient to cause damage in the growing thin film. The substrate temperature is typically maintained below 100°C without the need for direct cooling. The thin films exhibit bulk optical properties, they are also dense and super-smooth (<1nm rms roughness). The thin films also have typically low compressive stress. The magnetron targets are simple metals and are converted to compound thin films by using the appropriate reactive gas. The deposition process is high rate using pulsed dc power.

This paper provides data derived from a high throughput batch system with a 0.75m diameter drum substrate carrier and eight 1.2m linear magnetrons. The process geometry

is scaleable and adaptable to roll to roll deposition. Examples of both active coatings using on polymer substrates including polycarbonate, PET and Polyimide will be included. Details and examples of a novel final stage metal patterning process will also be presented .

Authors Index

Bold page numbers indicate the presenter

— A —

Aarts, I.M.P.: PS2+PV-MoM8, 12
Abdulgalil, A.G.M.: SS1-WeA2, 156
Abdulhalim, I.: TF-ThP31, 229
Abdulkadhim, A.: TF-ThM3, 184
Abel, J.R.: AS-WeM9, 120; MI-ThP1, **214**
Abell, C.: AS2+BI-ThM4, 166
Abelson, J.R.: AS+EM+MS+TF-MoA8, 24; TF2-TuM1, **63**; TF-WeA11, 160
Abernathy, C.: MI+EM-WeA4, **150**; VT-TuP10, 115
Abou Rich, S.: AS+NS-TuA3, 67
Abraham, B.: SE2-MoM4, 14
Abramson, J.: BI+AS+NS-FrM3, 234
Abstreiter, G.: BI+AS+BM+MS-WeM11, 121
Abu Haija, M.: NS-ThM1, 175; SS-ThP5, 220
Acharya, D.: MI+EM-WeA8, 151; SS2-MoM5, **18**
Adachi, T.: EM2-TuM11, 50
Adam, P.: PS+MS-MoA3, **30**
Adamo, C.: EM2-TuM9, 49
Adams, J.: BI-ThP9, **210**
Adams, M.H.: HI-MoM3, **7**
Adams, R.D.: SS2-MoA9, 34
Adler, H.: SS2-ThA11, 207
Adles, E.J.: EM-ThM6, **168**; NS+TR-TuM6, 53; SS2-FrM1, 244
Aeppli, G.: AS2+BI-ThM4, 166
Agarwal, A.: PS1-TuM1, 53; PS1-TuM3, **53**
Agarwal, S.: TF2-TuA8, **85**; VT-TuP17, 116
Ager, J.W.: EM-ThA9, 192
Agnoli, S.: GR-MoM4, 5
Agresta, D.: AS-TuP21, **92**
Aguirre, B.: EM2-TuM1, **48**
Aguirre, C.M.: GR+EM+MS-TuM3, 51; NS-WeA9, 152
Aguirre-Tostado, F.S.: EM-TuA8, **69**
Ahn, C.H.: SS1+EM-MoA4, 32
Ahn, H.B.: TF-ThP35, 229
Ahn, J.H.: EM-WeM11, 123
Ahn, S.K.: PS-ThP13, **218**
Akimichi, H.: VT-TuP16, 116; VT-WeM11, 140
Aksoy, F.: IS+SS-ThM2, 170
Al Takriti, S.: PS-FrM2, 240
Albers, B.J.: NS-ThM9, 176; TR+NS-WeM2, 137
Albrecht, O.: MI+TF-ThA9, **195**
Albrecht, P.M.: GR-MoM6, **6**
Alcami, M.: SS2-ThA10, 207
Alexander, M.R.: AS-ThA11, 187; BI-MoA3, 25; IJ+BI+MN+SE+AS-ThM10, 169; IJ+BI+MN+SE+AS-ThM9, 169
Alexandrowicz, G.: SS2-WeA12, 158
Alexeenko, A.: TF1-TuA8, **84**
Ali, D.: GR+EM+MS-TuM6, 51
Alibart, F.: EM-TuP2, 96
Alizadeh, A.: PS-TuA12, 76
Allara, D.L.: BI+AS+NS-WeA9, **145**
Allen, S.: AS2+BI-ThM1, **165**; AS2+BI-ThM5, 166; BI-ThP20, 213
Allende, S.: MI+TF-ThA9, 195
Alling, B.: TF1-MoM8, 19
Allison, W.: SS2-WeA1, 157; SS2-WeA12, 158
Al-Mahboob, A.: SS1-FrM4, 242
Almquist, B.: BI+AS+NS-ThA7, **188**
Alnabulsi, S.S.: AS-ThA10, 187
Aloni, S.: SS2-MoA11, 35
Altman, E.I.: NS-ThM9, 176; SS1+EM-MoA4, **32**; TR+NS-WeM2, 137
Alvarado, S.F.: MI+EM-WeA12, **151**
Alvarez, R.: TF1-TuA7, **83**
Alvis, R.: TF2-MoM4, 20
Amir, E.M.: MN-ThP6, **216**
Amonette, J.E.: AS+NS-WeM5, 117
An, I.: EM-TuP20, 99
An, M.J.: MI+EM-WeA7, 150
Anderle, M.: BM-ThP4, **213**
Anders, A.: SE2-MoM8, **14**
Andersen, J.N.: SS1+EM-MoA7, 32
Anderson, D.G.: BI-MoA3, 25; IJ+BI+MN+SE+AS-ThM9, 169
Anderson, M.L.: AS-FrM10, 233
Anderson, S.: TF1+PV-MoA2, 35
Andreaus, B.: VT-MoA1, 40
Angelini, T.: BI-TuP4, 94
Anniyev, T.: IS+AS-ThA2, 193; IS+SS-ThM12, 171; SS3-TuA7, **82**
Anpo, M.: SE1-MoM1, 12
Anthony, J.E.: AS+EM+MS+TF-MoM9, 3
Antonelli, A.: PS1-ThA10, 201
Aoki, T.: AS-ThA8, 187
Aoki, Y.: GR+EM+MS-TuM5, 51
Appelbaum, I.: AS-WeM9, 120; MS+GR+MI-ThM3, 174
Arai, K.: VT-TuP16, **116**; VT-WeM11, 140
Arakawa, I.: TR+SS-TuA1, 86
Araki, H.: MN-ThP2, 215
Ardalan, P.: EM1+PV-TuM5, **47**
Arenas Alatorre, J.: AS-TuP29, 93
Arenholz, E.: MI+TF-ThA3, 194
Arens, E.: SE1-MoM9, 13
Arès, R.M.: VT-WeA2, 162
Aresta, G.: AS+EM+MS+TF-MoM2, 2; AS+EM+MS+TF-TuM1, **43**
Arey, B.: IS+AS-ThA8, 193
Arinaga, K.: BI+AS+BM+MS-WeM11, 121
Arjad, A.B.: NS+BI-MoM2, **7**
Arlinghaus, H.F.: AS-TuP13, **91**
Armacost, M.: PS1-MoM9, 10
Armbruster, B.L.: IS+AS-FrM3, 235
Armstrong, N.: NS1+PV-TuA12, 73
Árnadóttir, L.: BI-TuM5, 46; BI-TuP13, **96**
Arnal, V.: PS1-MoM11, 10
Arnold, J.C.: PS1-MoM8, 10
Arnold, P.C.: VT-MoA7, **41**
Arpa Sancet, M.P.: BI-TuA8, 68
Artemenko, A.G.: SS1+AS+TF-ThM4, 181
Aruga, T.: SS2-WeA2, 157; SS-TuP2, 111
Arumainayagam, C.: SS1+PS+TF+AS+NS-TuA11, 80
Arwin, H.: AS+EM+MS+TF-MoA1, **24**; AS+EM+MS+TF-MoA11, 25; AS-TuP17, 92; AS-TuP19, 92
Aryal, M.: NS1+PV-TuA3, **72**
Asano, H.: GR+EM+MS-TuM12, **52**
Ashby, P.: SS-ThP16, 222
Asher, S.E.: TF1+PV-MoA6, 36; TF-ThA9, 208
Ashok, S.: TF1-MoM9, 19; TF-ThP23, **227**
Aspnes, D.E.: AS+EM+MS+TF-MoM10, 3; AS+EM+MS+TF-TuM3, **43**; AS-TuP3, 89; EM-ThM6, 168; NS+TR-TuM6, 53; SS2-FrM1, 244; TF-ThM10, 185
Asscher, M.: SS2-TuM11, **61**; SS3-TuA10, 83; SS-TuP1, 111
Athavan, N.: SS2-MoM11, **18**
Atiser, A.: SE-TuM3, 58
Atmaja, B.: BI-TuM11, **46**
Atodiresei, N.: MI-FrM4, 237
Attygalle, D.: AS+EM+MS+TF-TuM11, 44
Atuchin, V.: NS-TuP5, 101
Auciello, O.H.: MN+GR-ThM10, 174; MN+GR-ThM6, 174; MN+GR-ThM9, 174
Auerbach, D.J.: SS2-WeA11, **158**
Avouris, P.: GR+TF-TuA7, **71**
Awadelkarim, O.O.: EM-WeA3, 146
Aweda, T.A.: BI+AS+NS-WeA12, 145
Awo-Affouda, C.: MI+EM-WeA9, 151
Aydil, E.S.: EM1+PV-TuM4, **47**
Ayyaswamy, V.: TF1-TuA8, 84
Azarnouche, L.: PS1-TuM5, **54**
Azucena, O.: IJ+BI+MN+SE+AS-ThM5, 169

— B —

Baba, T.: TF-ThP27, 228
Babaeva, N.Yu.: PS-FrM1, **239**
Babar, S.: TF-WeA11, **160**
Bachand, G.: BM+MN+MS+TF+BI-ThA3, 189
Baddorf, A.P.: EM2-TuM6, 49
Baer, D.R.: AS+NS-WeM11, 118; AS+NS-WeM5, **117**; AS+NS-WeM9, 118; AS-TuP23, 92; AS-WeM12, 120; IS+AS-ThA8, 193
Baer, M.: SS1-WeA9, 156
Bagus, P.S.: SS2-WeM12, **135**
Bailey, K.: BI+AS+NS-ThA6, 188
Bailly, F.: PS1-MoM10, 10
Baio, J.E.: BI-ThP18, **212**
Bak, J.H.: MN+GR-ThM3, 173
Baker, R.: NS-WeM6, 127
Baklanov, M.R.: PS2-ThA11, 203; PS-TuA7, 75
Balaz, S.: SS1-FrM9, 243
Baldo, M.A.: EN-WeA9, **147**
Baldwin, J.: MN-FrM4, 238
Balema, V.E.: BI+NS-MoM2, 4
Ballav, N.: BI+AS+NS-ThA10, 189; NS+BI-MoA6, **29**; SS2-ThM5, 183
Bally, M.: BI+AS+NS-ThA6, **188**
Banba, A.: EM2-TuM11, 50
Banerjee, P.: NS1+PV-TuA4, 73; NS-WeM10, 127; NS-WeM3, 126
Banna, S.: PS1-TuM1, **53**
Bao, W.: GR+MI-WeM6, 125
Baraket, M.: GR-MoM5, 5; GR-TuP1, **100**; PS-TuA2, 75
Barankin, M.: SE-MoA4, 31
Barankova, H.: SE-MoA3, 31
Barbara, P.F.: EN-WeA3, **147**
Barbee, T.W.: TF1-TuA10, 84
Bardos, L.: SE-MoA3, **31**
Bareno, J.: GR+AS-WeA3, 148
Bareño, J.: TF1-MoM8, 19
Bargar, J.: IS+AS-ThA2, 193
Baricuatro, J.H.: SS2-WeM6, 134
Barja, S.: GR+AS-WeA7, 148; GR+TF-TuA4, 71
Barlow, D.E.: BI-TuA9, **68**
Barnett, S.A.: TF1+SE-TuM11, 63
Barrie, J.D.: TF2-MoA10, 39
Barry, P.: TR+SS-TuA9, 87
Barsoum, M.: AS-TuP19, 92
Bartels, L.: SS2-WeA7, **158**
Bartelt, N.C.: GR+AS-WeA9, 148; GR+TF-TuA9, 72; SS1-WeM11, 133; SS-ThP18, 222
Barth, J.V.: SS2-ThA3, **206**
Bartlett, A.J.: VT-MoM8, 22
Bartlett, B.M.: MI-FrM3, 236
Barton, D.: AS+EM+MS+TF-MoA9, 25
Barton, R.A.: MN-FrM8, **239**
Bartos, G.: IJ+MN+TF-WeA9, **149**
Bartynski, R.A.: SS2-TuA11, 81; SS2-TuM5, 60
Baruah, T.: MI-FrM3, 236
Basaran, O.A.: IJ+BI+MN-WeM9, **125**
Baski, A.A.: SS2-TuA3, **80**; TF-ThM6, 185
Bastos, K.P.: EM2-TuM3, 49; EM-TuA11, **70**
Batan, A.: PS2+TF-WeM1, **129**; PS2+TF-WeM10, 131
Batchelor, D.: BI-TuM4, 45
Bates, J.: MI-ThP3, **214**
Battaglia, G.: BM+MN+MS+TF+BI-ThA10, 190; BM+MN+MS+TF+BI-ThA4, 190
Battaile, C.C.: TR+SE-WeA10, **162**
Batyrev, I.: EM-WeA2, 145
Bäumer, M.: NS-WeM5, 126
Bausells, J.: TF-ThA11, 208
Baxter, J.: TF2-MoA7, 38
Baykara, M.Z.: NS-ThM9, 176; TR+NS-WeM2, **137**
Bayraktaroglu, B.: AS-TuP21, 92
Beatty, T.J.: EM1+PV-TuM4, 47

Bebensee, F.: SS2-WeM6, 134
Becerra-Toledo, A.E.: SS1-WeA10, **156**
Beck, K.M.: IS+SS-ThM6, 171
Becker, C.: SS1-TuM10, 59; SS2-TuM10, 61
Bedell, A.R.: TF-ThM9, 185
Bedzyk, M.J.: IS+AS-FrM1, 235
Beebe Jr, T.: BI-MoA7, **26**
Beebe, T.: BI-MoA8, 26
Beerbom, M.M.: EM-TuP11, 97; SS1-TuM1, 58
Behafarid, F.: NS-TuP14, **102**
Behera, S.: PS1-MoM3, 9
Behm, R.J.: SS2-ThA9, 206; SS2-ThM11, 184
Belashchenko, K.: MI+EM-WeA7, 150
Bell, W.: PS-TuA12, 76
Bellan, L.: MN-FrM3, 238
Bellitto, V.J.: SS1+AS+TF-ThM9, **182**
Belostotskiy, S.G.: PS2-TuM9, **56**
Belot, J.: EM-WeM6, 122
Belyansky, M.: TF-WeA7, **159**
Bender, H.: PS-TuA7, 75
Benjamin, K.: TR+NS-WeM11, 138
Benjamin, N.: PS1-TuM10, 54
Benlahsen, M.: EM-TuP2, 96
Benndorf, C.: TF-WeM6, 136
Bennethum, K.: AS+NS-WeM2, 117
Bennett, S.D.: EM-ThA1, 191
Benoit, D.S.W.: AS-ThA2, 186
Bent, S.F.: EM1+PV-TuM5, 47; SS1-MoM1, 15; SS1-MoM2, 15; TF-ThP33, 229
Bera, K.: PS1-WeA9, **154**; PS2-ThM1, 179
Berbil-Bautista, L.: SS-ThP4, 220
Bergeson, J.: TF-WeA2, 159
Bergmann, U.: IS+AS-ThA2, 193
Bermudez, V.: SS1+AS+TF-ThM3, **181**
Bernasek, S.: TF-WeM1, 135
Berry, J.: AS-FrM6, 232; TF-WeA2, 159
Bersch, E.: EM2-TuM2, **49**; MI-ThP1, 214
Bertino, M.F.: TF-ThM6, **185**
Bertrand, J.A.: TF2-TuA2, **84**; TF-WeA8, 160
Bertrand, P.: AS-TuP13, 91; PS-FrM8, 241; PS-TuP16, 108
Berube, P.-M.: PS2-ThA3, 202
Bérubé, P.-M.: PS-TuA1, **74**
Besacier, M.: NS-ThA4, 199
Besenbacher, F.: SS3-TuA8, 82
Bettac, A.: NS-ThA6, 199
Bevilacqua, C.: PS-ThP16, **219**
Beyer, A.: SS2-ThM12, 184
Bhadj Hamouda, A.: SS1-ThA4, 204
Bhadrachalam, P.: BI+NS-MoM6, **4**; NS+BI-MoM11, 9; NS-WeM12, 127
Bhandari, H.B.: TF2-MoM10, **21**
Bharadwaja, S.S.N.: TF1-MoM9, 19
Bhatti, A.S.: SS-TuP13, 113
Bhoj, A.: SS1-FrM8, **243**
Bhushan, B.: BM-ThP2, 213; MN-ThP3, 215; MN-ThP4, 215; TR+SS-TuA11, 87
Bianco, G.V.: BI+NS-MoM1, 4; SS2-TuA1, 80
Biener, J.: NS-WeM5, **126**; TF2-TuM12, 65
Biener, M.M.: NS-WeM5, 126; TF2-TuM12, **65**
Birch, J.: TF1-MoM8, 19
Bishop, S.R.: SS1+EM-MoA10, 33; SS1+EM-MoA3, 32; SS2-WeM2, **133**
Biswas, S.: IJ+BI+MN+SE+AS-ThM12, 170
Blake, M.: AS+NS-TuA9, 68
Blanchard, V.: PS-FrM9, 241
Blau, H.M.: BI-MoA1, 25
Blaze, M.: AS-TuP5, 89
Block, I.: SE+TF-TuA1, 76
Block, M.: PS2-ThM11, 180
Blomfield, C.J.: AS-ThA1, 186; EW-TuL5, 66
Blomquist, J.E.: SS1-WeA4, 156
Blouch, S.: EW-TuM8, 50; VT-MoA6, 41; VT-TuP4, 114
Blügel, S.: MI-FrM4, 237
Bluhm, H.: IS+AS-ThA9, 194; IS+SS-ThM1, 170; IS+SS-ThM11, 171; IS+SS-ThM2, 170; IS+SS-ThM5, 171; SS1-WeM4, 132; SS3-TuA8, 82; SS-TuP8, 112
Blunt, M.: BI-ThP20, 213
Bode, M.: GR-TuP4, 100
Bogart, K.H.A.: SS3-TuA9, 82
Bokor, J.: IJ+MN+TF-WeA1, **149**
Boland, T.: IJ+BI+MN+SE+AS-ThM3, **169**
Bonander, J.R.: SS1-WeM1, 131
Bonnell, D.A.: NS1+PV-TuA4, 73; NS-WeM10, 127; NS-WeM3, **126**
Booker, T.: NS-WeA3, 152
Booth, J.-P.: PS2-ThA1, **202**
Borca, B.: GR+AS-WeA7, 148; GR+TF-TuA4, **71**
Borca, C.: BI+AS+NS-FrM6, 234
Borgström, M.T.: SS1+EM-MoA7, 32
Borondics, F.: IS+SS-ThM5, **171**; SS3-TuA8, 82; SS-TuP8, 112
Bosnick, K.: TF-WeA4, **159**
Bostwick, A.: SS-TuP11, 113
Bouchoule, S.: PS2-ThA8, 203
Boudreault, O.: PS2-ThM10, **180**
Boufnichel, M.: PS1-TuM12, 55
Boullart, W.: PS2-ThA11, 203; PS-TuA7, 75
Boulmedias, F.: TF2-MoA4, 38
Bouten, P.C.P.: TF-FrM1, 246
Bouyssou, R.: PS1-MoM11, 10; PS1-MoM5, **9**
Bowers, J.E.: EN-WeM11, **123**
Boyd, D.: TF-ThP37, 230
Braam, K.: TF-ThP18, **226**
Bracker, A.S.: EM-ThA2, 191
Braganca, P.M.: GR+MI-WeM2, 124
Braje, D.A.: NS-ThA3, 198
Braly, L.: PS1-TuM10, 54
Brand, U.: MN+IJ+TR-ThA8, 196
Brash, J.L.: BI-TuM6, 46
Braun, K.-F.: EM-WeM3, 122
Braunstein, P.: BI+AS+NS-FrM6, 234
Bravenec, R.V.: PS2-ThM9, **180**; PS-ThP17, 219
Brede, J.: MI-FrM4, 237; SS-ThP8, 221
Bredin, J.: PS2-ThA1, 202
Breen, N.F.: BI-TuM9, 46
Breinlich, C.: SS2-TuM10, **61**
Breitling, F.: BI-ThP11, 211
Breitruck, A.: SS2-ThA9, 206
Brenes, D.A.: AS1-ThM9, **165**
Brennan, T.P.: EM1+PV-TuM5, 47
Brenning, N.: SE2-MoM6, 14
Bresin, M.: SS1+PS+TF+AS+NS-TuA2, **78**
Brett, M.J.: SE+TF-TuA9, 77; TF1+SE-TuM12, 63; TF-ThP17, 226
Breuer, S.: SS2-ThM2, **182**; SS2-ThM3, 182
Brink, J.: IS+AS-FrM3, 235
Brison, J.: AS-ThA2, **186**; AS-ThA3, 186; BI-TuM5, 46; BI-TuP13, 96
Broach, A.L.: SS1+AS+TF-ThM10, 182
Broekmann, P.: SS2-ThM2, 182; SS2-ThM3, 182
Broitman, E.: SE2-MoM3, 14; TR+SE-WeA1, **161**
Bromberg, V.: IJ+MN+TF-WeA10, **149**
Brongersma, H.: AS-FrM5, 232
Brouk, V.L.: PS1-WeM3, 128
Brown, A.S.: BI+NS-MoM1, **4**; NS-WeM9, 127; SS2-TuA1, 80
Brown, D.: PS-ThP2, 217
Brown, G.E.: IS+SS-ThM11, 171
Brown, I.G.: TF-WeM5, 136
Brown, J.: VT-MoA2, 40
Brown, Jr., G.: SS1-WeM4, 132
Brown, L.E.: BM+MN+MS+TF+BI-ThA4, **190**
Brown, M.A.: EM1+PV-TuM3, 47; SS1-WeM9, 132
Bruce, R.L.: PS-TuA10, **76**; PS-TuA12, **76**
Brucker, G.A.: EW-TuM8, 50; VT-MoA6, **41**; VT-MoA7, 41; VT-TuP4, 114
Brueck, S.R.J.: BI-ThP9, 210
Brugger, J.: TF-ThA11, 208; TF-WeM12, 137
Brundle, C.: AS-WeA10, **143**
Bruno, G.: BI+NS-MoM1, 4; NS-WeM9, 127; SS2-TuA1, 80
Bruns, M.: AS-TuP1, **89**
Brusciotti, F.: PS2+TF-WeM1, 129; TF2-MoA2, 37
Bryan, S.R.: AS1-ThM6, 164; AS-ThA9, **187**
Bryers, J.D.: BI-TuA3, **68**
Bucholz, E.: NS+TR-TuM2, **52**
Buck, M.: NS+BI-MoA7, 29; SS2-ThM6, 183
Budai, J.D.: MI+TF-ThA4, 194
Buergel, S.: BI+AS+NS-ThA6, 188
Bui, H.: BI-MoA7, 26
Bull, S.J.: TR+NS-WeM9, **138**
Bunker, K.L.: AS+NS-TuA4, **67**; AS+NS-WeM2, 117; EW-WeM8, 124
Burberry, M.S.: TF3-MoA8, 40
Burgess, Jr., D.R.: TF-ThP34, 229
Buriak, J.M.: SE+TF-TuA9, 77
Burke, S.: TF1-TuA11, 84
Burkett, S.L.: MN-FrM10, 239
Burk-Rafel, J.: BI-ThP8, 210
Burn, P.L.: TF-ThA2, 207
Burnham, N.A.: TR+NS-WeM6, **138**
Burst, J.: TF-FrM5, **247**
Bush, B.: TR+SE-WeA4, 161
Busnel, F.: PS-FrM9, 241
Bussmann, E.: SS1-ThA10, 205
Butcher, D.: IS+SS-ThM2, 170; SS2-MoA11, 35
Butterfield, M.T.: MI-ThM6, 173
Byun, J.S.: AS-TuP2, 89

— C —

Caballero, A.: IS+SS-ThM5, 171
Caffio, M.: GR+AS-WeA8, **148**; NS+BI-MoA7, 29
Cagin, E.: EM2-TuM10, **50**
Cahen, D.: NS1+PV-TuA11, 73
Cai, G.: NS-TuP31, **105**; SE1-MoM4, 13
Caldwell, J.: GR+SS-MoA3, 27
Call, N.: EM-TuP6, 97
Callahan, K.: SS1-WeM9, 132
Calle, C.: SE1-MoM9, 13
Camara, C.B.: TR+SS-TuA3, 87
Cameron, L.G.: SS3-TuA3, 81
Camillone, N.: SS2-WeM3, 133
Campagna, L.: VT-WeM9, 140
Campbell, C.T.: SS2-WeM6, 134; SS3-TuA3, **81**
Campbell, P.M.: GR+EM+MS-TuM4, 51; GR+SS-MoA3, 27; GR+TF-TuA3, 71
Campbell, V.L.: SS2-WeA10, 158
Canavan, H.E.: BI-TuP4, 94
Cannara, R.J.: TR+NS-WeM5, 138
Cansizoglu, M.F.: TF1+SE-TuM4, **62**
Cao, J.X.: MI+TF-ThA3, 194
Cao, X.: BI-TuA8, 68
Cao, Y.: MS-ThA4, 197
Caperton, R.J.: TF-ThM6, 185
Capezzuto, P.: SS2-TuA1, 80
Capriotti, L.: BI-MoA7, 26
Caquineau, H.: PS2-TuM3, 56
Carach, C.: NS-ThM10, 176
Cardenas, J.: NS+BI-MoM9, 8
Carney, T.: AS-FrM7, 233
Carpick, R.W.: TR+NS-WeM5, 138
Carraro, C.: GR+SS-MoA11, 28; IS+AS-FrM10, 236; MN+IJ+TR-ThA1, **196**; MN+IJ+TR-ThA4, 196; TR+SE-WeA4, 161
Carrere, M.: PS1-ThA1, 199
Carrizales, C.E.: SS-ThP9, 221
Carroll, M.S.: EM1+PV-TuM11, 48; EM-TuP5, 97
Carter, D.: PS1-WeM3, **128**
Carton, O.: TF-WeA9, **160**
Cartry, G.: PS1-ThA1, **199**
Caruso, A.N.: MI-FrM7, 237; MI-FrM8, 237; MI-ThP4, **214**
Castell, M.R.: SS2-MoM1, 17
Castle, J.E.: AS-WeM12, 120
Castner, D.G.: AS+NS-WeM4, 117; AS+NS-WeM9, 118; AS-ThA2, 186; AS-ThA3, 186; BI+AS+NS-ThA9, **189**; BI-ThP13, 211; BI-ThP18, 212; BI-TuM5, 46; BI-TuM9, 46; SS2-FrM6, 245
Casuccio, G.: AS+NS-TuA4, 67
Cattani, M.: TF-WeM5, 136
Cavalero, R.: GR+SS-MoA7, 27

Cavanagh, A.S.: TF2-MoM3, 20; TF2-TuA9, 85; TF3-MoA6, **39**
Cederberg, J.G.: EM1+PV-TuM11, 48; EM-TuP5, 97
Celik, O.: GR-MoM4, 5
Cerda, J.I.: SS1-WeM12, 133; SS2-TuM1, 60
Cerruti, M.: GR+SS-MoA11, **28**; TF-ThM10, 185
Cha, C.: BI-TuP10, 95
Cha, J.N.: BI-TuM11, 46
Cha, Y.H.: AS-TuP2, 89
Chabal, Y.: MN-FrM9, 239; NS-WeM4, 126; SS1-MoM5, 16; SS1-MoM6, 16
Chace, M.: AS+EM+MS+TF-TuM12, 45
Chae, J.S.: GR+MI-WeM12, **125**
Chaffee, P.D.: TF2-MoA10, 39
Chakarov, D.: NS+BI-MoM9, 8
Chaker, M.: PS2-ThA3, 202; PS-TuA1, 74
Chakraborty, S.: BI+NS-MoM5, **4**
Chamberlin, S.E.: SS2-MoM2, **17**
Chambers, S.A.: AS-TuP23, 92; SS1-MoM8, 16; TF1+PV-MoA4, 36
Champness, N.R.: NS+BI-MoA7, 29
Chan, C.K.: VT-WeA12, 163
Chan, K.: NS+BI-MoM1, 7
Chandrasekhar, N.: EM-WeA9, 146
Chandross, M.: TF-ThA10, **208**
Chang, C.C.: PS-ThP8, **218**; VT-WeA12, 163
Chang, C.H.: PS-ThP19, **220**
Chang, C.-M.: NS-TuP23, 104; TF-ThP43, 231
Chang, H.T.: SE1-MoM5, 13
Chang, H.W.: PS-ThP18, **219**; PS-TuP12, 107
Chang, H.Y.: PS-ThP13, 218; PS-ThP14, 219
Chang, J.: EM-ThA11, 192; PS1-WeA4, **153**; TF2-TuA11, 86
Chang, K.: GR+AS-WeA11, 149
Chang, S.: PS1-ThM6, **177**; SS2-ThA8, 206; SS-ThP8, **221**
Chang, Y.C.: AS-TuP2, 89; AS-TuP3, 89
Chang, Y.L.: PS-ThP19, 220
Chao, A.: NS2-TuA2, 74
Char, K.: MN+GR-ThM3, 173
Chau, S.W.: PS-ThP7, 217
Chawla, J.S.: TF2-MoA8, **38**
CheGal, W.: BI+AS+NS-WeA11, 145
Chen, C.-F.: PS1-ThM11, 178
Chen, C.L.: PS-TuP12, 107; VT-WeA12, 163
Chen, D.A.: SS2-MoA8, **34**
Chen, E.: MI+TF-ThA8, 195
Chen, F.: BI-ThP18, 212
Chen, F.R.: NS-TuP23, 104
Chen, H.P.: TF-ThP22, 227
Chen, J.: AS+EM+MS+TF-TuM11, 44; PS1-MoM8, 10; VT-MoM5, 22
Chen, J.-H.: GR+SS-MoA4, **27**
Chen, J.R.: VT-TuP13, 115; VT-WeA12, **163**
Chen, L.: PS2-ThA4, 202; PS2-ThM2, 179; PS2-ThM9, 180; PS-ThP17, 219; TF1-MoM10, 20
Chen, M.: EM-TuP16, **98**
Chen, M.S.: SS1-MoM11, **17**
Chen, N.: MN+IJ+TR-ThA10, 197; SS2-WeA10, 158
Chen, P.: EM-TuA7, 69
Chen, P.L.: NS-TuP26, 104
Chen, S.: PS1-WeM11, **129**
Chen, S.J.: NS-TuP23, **104**
Chen, W.: EM-ThM10, **168**
Chen, W.-C.: EM-TuP1, **96**; TF-ThP26, 228
Chen, Y.: EM-ThM10, 168; EM-ThM11, 168; EM-ThM12, 169; NS-TuP31, 105; SE1-MoM4, **13**
Chen, Z.: PS-ThP5, **217**
Chen, Z.Y.: PS2-ThA4, **202**
Cheng, C.: SE1-MoM4, 13
Cheng, C.M.: VT-TuP13, 115; VT-WeA12, 163
Cheng, F.: BI-ThP8, **210**; BI-TuM5, 46
Cheng, H.-Y.: PS1-ThM11, 178
Cheng, M.H.: SS2-ThM9, **183**; SS-ThP16, 222
Cheng, S.L.: EM-TuP19, 99
Cheng, Z.: SS2-WeA7, 158
Cheon, H.: EM-TuP20, **99**
Chera, J.C.: AS-TuP24, 93
Cherkashinin, G.: SS2-ThM2, 182
Cheung, W.S.: VT-TuP15, 115; VT-TuP6, **114**
Chevolleau, T.: PS1-MoM10, 10; PS1-MoM11, 10; PS1-MoM5, 9
Chhowalla, M.: GR-MoM4, 5
Chi, E.: BI-TuP7, 94
Chiang, S.: SS1-ThA9, 205
Chiang, W.-H.: PS2-TuM1, 55
Chichkov, B.N.: TF-WeM3, 135
Chidambarrao, D.: TF-WeA7, 159
Chiggiato, P.: VT-WeA9, **163**
Childress, J.R.: MI+TF-ThA1, **194**
Chilkoti, A.: BI+AS+BM+MS-WeM9, **121**; BI+AS+NS-WeA10, 145; BI-ThP12, 211; BI-ThP16, 212; BI-TuP5, 94; BI-TuP7, 94
Chinn, J.D.: TR+SE-WeA11, 162
Chirita, V.: TF1-TuA4, **83**
Chistyakov, R.: SE2-MoM4, 14
Chitre, K.: SS2-TuA11, 81
Chiu, P.: TR+SS-TuA9, 87
Chiu, P.K.: TF-ThP22, 227
Chiu, Y.P.: SS1-ThA11, **205**
Cho, B.C.: TF-ThP35, 229
Cho, B.J.: GR-MoM3, 5
Cho, H.: BI+AS+NS-WeA11, 145
Cho, J.: SS-ThP4, **220**
Cho, K.: SS1-MoM5, 16
Cho, M.-H.: AS1-ThM12, 165
Cho, S.: EM-TuP18, 98
Cho, S.H.: PS-TuP2, 105
Cho, S.U.: MI-ThM2, **172**
Cho, W.H.: EM-TuP3, 96; TF-ThP22, 227; TF-ThP30, 229
Choi, B.Y.: SS1-WeM10, **132**; SS-ThP11, 221
Choi, C.: BI-TuP6, **94**
Choi, H.K.: MI-ThM2, 172
CHoi, H.Y.: VT-TuP15, 115
Choi, J.W.: MN+GR-ThM4, **174**
Choi, M.S.: PS1-WeA11, 154
Choi, S.G.: AS+EM+MS+TF-MoM1, **2**
Choi, S.I.: PS-TuP15, 108
Choi, Y.D.: EM-TuP23, 99
Chong, C.H.: MS-ThA1, 197
Chopra, I.S.: SS1-MoM5, **16**; SS1-MoM6, 16
Chou, K.: EM-ThM11, 168
Choudhary, G.K.: PS1-ThA9, **201**; PS-TuA12, 76; PS-TuA9, 75
Chowdhury, S.: NS+BI-MoA3, 28
Christensen, S.T.: TF2-MoM6, 21
Christopher: SS2-MoA3, **34**
Chu, C.: PS1-MoM8, 10
Chu, C.T.: TF2-MoA10, 39
Chu, N.N.: NS-TuP26, 104
Chueh, W.: TF1-TuA9, **84**
Chung, I.S.: NS-TuP7, 101; TF-ThP38, 230; TF-ThP39, 230; TF-ThP40, 230
Chung, K.B.: EM2-TuM9, 49; EM-TuA11, 70
Chung, S.M.: VT-MoM9, 23
Chung, T.-Y.: PS-TuA10, 76; PS-TuA9, **75**
Chung, Y.W.: TR+SE-WeA2, 161
Chwalek, J.: IJ+MN+TF-WeA7, 149
Chyi, J.-I.: EM-ThA6, **191**
Ciftlikli, E.Z.: SS2-TuM5, **60**
Ciobanu, C.V.: GR+AS-WeA3, 148; VT-TuP17, 116
Claessens, C.: SS1-FrM2, 242
Claridge, S.A.: EM-TuP26, 99
Clark, A.: NS-WeA3, 152
Clark, K.: EM-WeM3, 122; MI+EM-WeA8, **151**; SS2-ThA8, 206
Clark, N.J.: GR+TF-TuA10, 72
Clark, R.: EM2-TuM2, 49
Clark, T.: BI-TuM3, 45
Clavero, C.: MI-ThM1, 172
Clemens, J.B.: SS1+EM-MoA3, **32**
Clerk, A.A.: EM-ThA1, 191
Cloud, A.N.: SE2-MoM11, **15**
Cobet, C.: AS+EM+MS+TF-TuM6, **44**
Cockins, L.P.: EM-ThA1, **191**
Coclite, A.M.: TF-WeA10, **160**
Cohen, S.: PS2+TF-WeM3, 130
Cohen, S.R.: BI-ThP6, **210**; TR+SS-TuA10, 87
Cojocaru, C.V.: MI-ThP3, 214
Coker, E.N.: SS3-TuA9, 82
Colavita, P.: SS2-FrM5, 245
Coles, J.: BI-TuP10, **95**
Colesniuc, C.N.: EM-TuP13, 98
Collier, G.: BI-TuP12, **95**
Collings, M.P.: SS1-WeA1, 155; SS1-WeA2, 156
Collins, K.: PS1-TuM1, 53; PS1-TuM3, 53; PS1-WeA7, 153; PS1-WeA9, 154; PS1-WeM5, 128; PS2-ThM1, 179; PS-ThP5, 217
Collins, R.W.: AS+EM+MS+TF-MoA6, **24**; AS+EM+MS+TF-TuM11, 44
Colombo, L.: GR+AS-WeA10, 148
Colpo, P.: AS2+BI-ThM6, 166; BI+AS+NS-FrM5, 234
Coltrin, M.E.: SS3-TuA9, 82
Conard, T.: AS-WeA1, **142**
Conklin, D.: NS1+PV-TuA4, 73; NS-WeM10, **127**; NS-WeM3, 126
Conley, H.J.: BI-ThP2, 210
Conrad, M.: SS1-TuM1, 58
Consiglio, S.: EM2-TuM2, 49
Conti, G.: AS-WeA10, 143; AS-WeA9, **143**
Conti, R.: TF-WeA7, 159
Contreras-Guerrero, R.: EM-TuA10, 70
Cooper, M.: AS2+BI-ThM4, 166
Cooper-White, J.J.: BI-TuP11, 95
Coronado, E.: MI-FrM5, 237
Cossement, D.: TF2-MoA2, 37
Cotrino, J.: TF1-TuA7, 83
Coulter, K.: NS+BI-MoM1, **7**
Coutts, T.J.: TF1+PV-MoA10, 37
Craighead, H.: MN-FrM3, 238; MN-FrM4, 238; MN-FrM5, 238; MN-FrM8, 239; NS+TR-TuM5, 53
Creatore, M.: AS+EM+MS+TF-MoM2, **2**; AS+EM+MS+TF-TuM1, 43; EM1+PV-TuM12, 48; PS2-TuM5, 56; PS-TuP10, 107; TF2-TuM11, 64; TF-ThA8, 208
Creighton, J.R.: SS3-TuA9, **82**
Cremer, R.: SE2-MoM1, **14**
Cress, C.D.: EM-ThA2, 191
Crist, V.: AS1-ThM1, **164**
Crommie, M.F.: MI-FrM3, 236; SS-ThP4, 220
Cross, J.: MN-FrM4, **238**
Cross, K.C.: SS3-TuA9, 82
Croy, J.: SS-TuP6, **112**
Cucchiara, J.: MI+TF-ThA6, 194
Cuddy, M.: PS1-ThA4, **200**
Cuenya, B.R.: SS2-MoA6, **34**
Cui, X.: BI-MoA9, **26**
Culbertson, J.C.: GR+TF-TuA3, 71
Cullen, W: GR+SS-MoA4, 27
Cumpson, P.: AS-WeA4, **142**
Cunge, G.: PS2-ThA6, 202
Cunningham, B.T.: SE+TF-TuA1, 76
Curley, G.A.: PS2-ThA1, 202; PS2-ThA8, **203**
Curri, M.L.: NS+BI-MoM3, **7**
Cyganik, P.: NS+BI-MoA10, 30; NS-TuP29, **104**
Czigány, Z.: TF1-MoM8, 19
Czigany, Zs.: TR+SE-WeA1, 161

— D —

da Silva, F.: NS-ThA3, **198**
Dadson, A.: TF2-MoA1, 37
Dagata, J.A.: AS2+BI-ThM10, 167
d'Agostino, R.: PS2+TF-WeM6, 130; PS2-TuM2, 55; TF-WeA10, 160
Dahal, L.R.: AS+EM+MS+TF-MoA6, 24
Dahint, R.: BI-ThP11, **211**
Dahlin, A.: BI+AS+NS-WeA3, 144
Dai, L.: TF-WeA4, 159
Dai, Z.: NS+BI-MoM5, 8
Daimon, H.: AS-WeA11, 143
Dameron, A.: TF-WeA2, 159
Dams, R.: PS-TuP10, 107

Dao, N.: SS1-MoM5, 16; SS1-MoM6, 16
Darlak, A.: PS1-MoM9, 10; PS-TuP3, 106
Darling, S.B.: MN+GR-ThM6, 174; NS1+PV-TuA7, **73**
Dasaka, R.K.: PS1-ThM11, 178
DaSilva, F.: MI-ThM2, 172
Dave, S.R.: AS+NS-WeM4, 117
Davia, D.: NS-TuP1, 100
David, J.M.: SS-ThP17, 222
David, T.: PS1-MoM10, 10; PS1-MoM11, 10; PS1-MoM5, 9
Davies, M.C.: AS-ThA11, 187; BI-MoA3, 25; IJ+BI+MN+SE+AS-ThM9, 169
Davies, R.: MI+EM-WeA4, 150; VT-TuP10, **115**
Davila, S.: SS1-FrM6, 243
Davis, B.S.: BI-ThP2, **210**
Davis, K.: MS-ThA8, 198; SE1-MoM9, 13; TF-ThP42, **230**
Davis, R.C.: BI-ThP2, 210; MN+GR-ThM5, 174; NS+BI-MoA4, 29; NS2-TuA8, 74; SS2-FrM4, 244; TF2-MoA1, 37; TF2-TuM5, 64; TF-WeM11, 136
Day, C.: VT-WeA3, 162
D'Costa, V.: AS-TuP32, **93**
De Graeve, I.: PS2+TF-WeM1, 129
de Heer, W.A.: GR+EM+MS-TuM9, **52**
de Jong, A.F.: SS1+PS+TF+AS+NS-TuA8, 79
de la Figuera, J.: SS2-TuM1, 60
de Laat, HB.: BI-MoA9, 26
De las Heras, E.: SE-TuP6, 110
de Smit, E.: IS+AS-ThA3, **193**
de Vries, H.: AS+EM+MS+TF-TuM1, 43; PS2-TuM5, 56
Decaluwe, S.C.: IS+AS-ThA9, 194
Decker, A.: NS2-TuA1, 73
Degendt, S.: PS2-ThA11, 203
Degiron, A.: BI+AS+NS-WeA10, 145
Dekhter, R.: EW-TuA6, **70**
Dekker, J.: PS2+MN-WeA2, **154**
DeKoven, B.M.: TR+SE-WeA11, 162
Delcorte, A.: AS-TuP13, 91
Dellas, N.S.: EM-WeA3, 146
DeLongchamp, D.M.: AS+EM+MS+TF-MoM9, 3
Demaree, J.D.: TF2-TuA3, 85
Demirel, M.C.: TF1+SE-TuM5, **62**
Denis, L.: TF2-MoA2, **37**
Deniz, D.: TF1+SE-TuM10, **63**
Deodeshmukh, V.: SS1-FrM10, 244
Derenge, M.: EM-WeA2, 145
Deriy, A.: AS+NS-TuA1, 67
Desai, T.A.: TF-ThM11, **185**
Desai, T.V.: SS1-FrM3, **242**
DeSario, P.A.: SE1-MoM3, **12**
Desikan, R.: TF-ThM1, **184**
DeSimone, J.M.: BP+NS-SuA1, **1**
Desjardins, P.: GR+EM+MS-TuM3, 51; NS-WeA9, 152
Deskins, A.: SS2-MoM8, 18; SS2-WeM10, 134
Despont, M.: TF-WeM2, 135
Devarajan, S.P.: SS1-TuM11, 59
Devine, B.: TR+SS-TuA8, 87
Dhayal, M.: BI-ThP3, **210**; BI-ThP8, 210
Dhere, R.G.: TF1+PV-MoA6, 36; TF-ThA9, **208**
Di Pasquale, J.: GR+EM+MS-TuM6, 51
Di, M.: EM2-TuM2, 49
Diaconescu, B.: SS2-ThA6, **206**
Diao, L.: PS1-TuM11, **55**
Dias da Silva, L.G.G.V.: MI-FrM6, 237
Dickey, E.C.: AS+EM+MS+TF-MoM5, 2; AS+EM+MS+TF-MoM6, 2
Dickinson, G: BI-TuA9, 68
Dickinson, T.: EM-ThM9, 168
Dictus, D.: PS2-ThA11, **203**
Diebold, A.C: EM2-TuM2, 49; MI-ThP1, 214
Diebold, U.: EM-ThM5, 168; SS2-MoM3, **17**
Diederich, F.: SS2-ThA1, 205
Dietzel, D.: TR+NS-WeM1, **137**
Dil, H.: SS2-ThA7, 206
Dilabio, G.: NS-WeM11, 127
Dillon, A.C.: TF3-MoA6, 39
Dilonardo, E.: PS2+TF-WeM6, 130
Dilullo, A.: SS2-ThA8, 206
Dimitrakopoulos, C.: PS2+TF-WeM3, 130
Ding, G.: PS-TuP1, **105**
Dingemans, G.: SS2-FrM2, 244; TF3-MoA7, 39
Dissing, D.A.: MN+GR-ThM9, 174
Divan, R.: MN+GR-ThM9, 174; MN-FrM10, 239
Djayaprawira, D.D.: TF-ThA3, 207
Dluhy, R.D.: SE+TF-TuA3, 77
Dohnalek, Z.: SS2-MoM8, 18; SS2-WeM10, 134
Dohnálek, Z.: SS1-WeA9, 156
Dong, X.: AS-FrM3, **232**
Donnelly, V.M.: PS1-ThA6, **200**; PS2-ThA4, 202; PS2-ThM10, 180; PS2-TuM9, 56
Donoso Barrera, A.: AS2+BI-ThM4, 166
Doom, L.: VT-WeA11, 163
Doran, A.: BI-TuM6, 46
Doren, D.: SS2-FrM9, **245**
Dorf, L.: PS1-WeA9, 154; PS1-WeM5, **128**; PS2-ThM1, 179
Dorsman, R.: VT-WeM6, 139
Doudin, B.: BI+AS+NS-FrM6, 234
Douhard, B.: PS2+TF-WeM1, 129
Dowben, P.A.: BI+AS+NS-FrM6, 234; MI+EM-WeA7, 150
Doyle, J.: PS-TuP19, 109; TF-ThP18, 226
Dragoi, V.: AS+EM+MS+TF-TuM2, 43; SE-TuP7, 110
Draper, D.: TF-ThP19, 226
Drawl, W.R.: TF1-MoM9, 19
Drechsler, U.: TF-WeM2, 135
Driver, M.S.: MI-ThP4, 214
Drobny, G.P.: BI-TuM9, 46
Droubay, T.: AS-TuP23, 92; TF1+PV-MoA4, 36
Drummond, I.W.: AS-ThA1, 186
Du, C.C.: PS-ThP19, 220
Du, Y.: SS2-MoM8, 18; SS2-WeM10, **134**; TF1-MoM10, 20
Duan, X.F.: TF2-MoA6, **38**
Dubey, M.: AS-ThA2, 186; BI+AS+NS-ThA9, 189; BI-ThP13, 211; BI-ThP8, 210; SS2-FrM6, **245**
Dubois, G.: AS+EM+MS+TF-TuM12, 45; PS2+TF-WeM3, 130
Dubreuil, M.: PS-TuP10, 107
Ducker, R.E.: BI-ThP16, **212**
Ducote, J.: PS1-MoM10, **10**
Duenow, J.N.: TF1+PV-MoA6, **36**; TF-ThA9, 208
Duerig, U.T.: TF-WeM2, 135
Dürr, M.: SS1+PS+TF+AS+NS-TuA12, **80**; SS2-FrM8, 245
Dufour, T.: PS2-TuM11, 57
Dugerjav, O.: SS-ThP1, 220; SS-ThP2, 220
Dugger, M.T.: MN+IJ+TR-ThA3, 196
Dunin-Borkowski, R.E.: SS1+PS+TF+AS+NS-TuA7, 79
Dunn, K.A.: SS1+PS+TF+AS+NS-TuA2, 78
Dupuis, M.: SS2-MoM8, 18; SS2-WeM10, 134
Durand, A.: SS1-ThA9, 205
Durand-Drouhin, O.: EM-TuP2, 96
Dussart, R.: PS1-TuM12, 55; PS2-TuM11, **57**
Duvjir, G.: SS-ThP1, 220; SS-ThP2, 220
Dvorak, S.D.: TR+SS-TuA2, 86
Dziomba, T.: MN+IJ+TR-ThA8, **196**

— E —

Eacobacci, M.J.: VT-MoM8, 22
Ecija, D.: MI-FrM5, **237**; SS2-ThA10, 207; SS2-ThM10, 183
Economou, D.J.: PS1-WeA1, **153**; PS2-ThA4, 202; PS2-TuM9, 56
Eda, G.: GR-MoM4, 5
Eddings, M.: BM+MN+MS+TF+BI-ThA6, 190
Eddy, Jr., C.R.: GR+EM+MS-TuM4, 51; GR+TF-TuA3, 71; SS2-TuA2, 80
Egelhoff, W.F.: MI+TF-ThA8, 195
Eichhorn, L.: PS2+PV-MoM4, **11**
Einstein, T.: SS1-ThA4, 204
Ekerdt, J.G.: AS+NS-WeM3, 117; TF2-TuA12, 86
El Gabaly, F.: IS+AS-FrM10, 236; IS+AS-ThA9, **194**
El Kodadi, M.: NS-ThA4, **199**
Elam, J.W.: IS+AS-FrM1, 235; TF2-MoM6, **21**
El-Dasher, B.S.: TF2-TuM12, 65
Ellefson, R.E.: VT-MoA3, **41**
Ellingboe, A.R.: PS2+PV-MoM11, 12; PS2-ThM4, **179**; PS-ThP6, 217
Ellis, J.: SS2-WeA1, 157; SS2-WeA12, 158
Emelli, E.: VT-WeM9, 140
Emoto, K.: BI+AS+NS-ThA9, 189; BI-ThP13, 211
Enache, I.: PS2-TuM3, 56
Enache, M.: SS2-ThA1, 205
Engelhard, M.H.: AS+NS-WeM5, 117; AS+NS-WeM9, 118; AS-TuP23, **92**; AS-WeM12, 120; EM2-TuM1, 48; NS-TuP32, 105; SS1-FrM10, 244; SS3-TuA11, 83
Engelken, R.: TF1+SE-TuM4, 62
Engeln, R.: AS+EM+MS+TF-TuM9, 44; PS1-ThA3, 200
Engin, S.: AS-TuP1, 89
Engstrom, J.R.: SS1-FrM3, 242; TF2-MoM11, 21
Eppler, A.: PS1-TuM10, 54
Epstein, A.J.: MI-FrM1, **236**
Eralp, T.: BI-TuM4, 45
Erdemir, A.: IS+AS-FrM9, 236; TR+SS-TuA12, **88**
Erickson, D.: BM+MN+MS+TF+BI-ThA1, **189**
Eriguchi, K.: NS+BI-MoA8, 29; PS1-ThA8, 201; PS1-ThM9, 178
Ermakov, A.V.: VT-MoA4, 41
Ermanoski, I.: SS-ThP18, **222**
Ernstoff, J.: EW-TuA6, 70; NS-ThA1, 198
Erwin, S.C.: NS-ThA8, 199
Eryilmaz, O.: IS+AS-FrM9, 236; TR+SS-TuA12, 88
Escaño, M.C.S.: SS-TuP10, 112
Escher, M.E.: AS-WeM2, 119
Escobar, J.V.: TR+SS-TuA3, 87
Esser, N.: AS+EM+MS+TF-TuM6, 44
Eum, K.H.: TF-ThP38, 230; TF-ThP39, **230**
Evans, J.: SS3-TuA1, 81
Evans, J.W.: SS1-ThA3, 204; SS2-WeM11, 134
Everitt, H.O.: NS-WeM9, 127
Everts, F.: AS+EM+MS+TF-MoM11, 3
Evoen, V.: NS+BI-MoA3, **28**
Exarhos, G.J.: TF1+PV-MoA4, 36

— F —

Facchetti, A.: TF-FrM3, **246**
Fadley, C.S.: AS-WeA9, 143
Fairbrother, H.: SS1+PS+TF+AS+NS-TuA1, **78**
Fanelli, F.: PS2-TuM2, **55**
Fang, F.: TF1+PV-MoA7, **36**
Fang, Y.: AS-TuP32, 93
Fanton, M.A.: GR+EM+MS-TuM4, 51; GR+SS-MoA10, **28**; GR+SS-MoA3, 27; GR+SS-MoA7, 27
Farkas, N.: AS2+BI-ThM10, **167**
Farrow, R.L.: IS+AS-ThA9, 194
Farruggia, G.: IJ+MN+TF-WeA11, 149
Faubel, M.: SS1-WeM9, 132
Fazio, G.: PS-ThP16, 219
Fdez-Sanz, J.: SS3-TuA1, 81
Fears, K.: BI-TuM3, **45**
Feenstra, R.: GR+SS-MoA6, 27
Feibelman, P.J.: GR+TF-TuA9, 72; SS1-WeM12, 133
Felgenhauer, T.: BI-ThP11, 211
Felmetsger, V.V.: TF-ThP1, **223**
Felten, A.: AS+NS-TuA3, 67
Felz, A.: NS-ThA6, 199
Fendt, L.-A.: SS2-ThA1, 205
Feng, J.: NS-TuP1, **100**
Feng, T.: EM-TuA3, 69; EM-TuA4, 69; EM-TuA9, 70
Feng, Z.: IS+AS-FrM1, **235**
Ferekides, C.S.: TF-ThP21, 227
Fernandes, P.: NS-WeM4, 126
Fernandez-Nieves, A.: IJ+BI+MN-WeM5, **125**

Fernsler, R.F.: PS-TuA2, 75
Ferralis, N.: GR+SS-MoA11, 28; IS+AS-FrM10, **236**
Ferreira, M.J.: VT-WeA10, **163**; VT-WeA11, 163
Ferrer, D.A.: NS-TuP5, 101
Ferris, R.: BI-ThP15, **212**
Feurprier, Y.: PS1-MoM8, 10
Fian, A.: SS1+EM-MoA7, 32
Field, D.A.: GR+TF-TuA10, 72
Filoti, D.I.: TF-ThM9, **185**
First, P.N.: NS-ThA8, 199
Fischer, D.A.: AS+EM+MS+TF-MoM9, 3; AS1-ThM11, **165**; TR+SE-WeA11, 162
Fischer, P.J.: MI-ThM9, **173**
Fischer, R.: TF2-MoA3, 37
Fisher, E.R.: PS1-ThA4, 200; PS1-ThM12, 178; PS2+TF-WeM9, 130; TF-ThM5, 185
Fisher, G.L.: AS1-ThM6, **164**; AS-ThA9, 187
Fisher, P.: GR+SS-MoA6, **27**
Flaherty, D.W.: AS+EM+MS+TF-MoA4, 24
Flauta, R.E.: PS1-WeM4, 128; SE2-MoM11, 15
Fleischer, S.: BI-ThP6, 210
Flores, M.: AS-TuP29, 93; SE-TuP6, **110**; TR-ThP2, 231
Floro, J.A.: NS2-TuA3, 74
Flynn, K.: VT-MoM10, **23**
Folgner, K.A.: TF2-MoA10, 39
Folks, L.: MI-ThM5, 172
Fölsch, S.: NS-ThA7, 199
Forster, S.: BM+MN+MS+TF+BI-ThA10, **190**
Fostner, S.: TF1-TuA11, 84
Foussekis, M.A.: SS2-TuA3, 80
Fowlkes, J.D.: TF-WeM4, 136
Fox, K.: MI+EM-WeA7, 150
Fracassi, F.: PS2+TF-WeM6, 130; PS2-TuM2, 55
Francis, S.: NS+BI-MoA7, 29
Franco, G.C.: NS+BI-MoM6, **8**; NS-TuP5, 101
Frank, C.W.: BI-TuM10, 46; BI-TuM11, 46
Franking, R.: SS1-MoM8, **16**
Frankland, V.L.: SS1-WeA1, **155**
Franquet, A.: PS-TuA7, 75
Frantz, E.: GR+SS-MoA7, 27
Franz, G.: PS-FrM7, **240**
Franzen, S.: NS+TR-TuM6, **53**; TF-ThM10, 185
Franzka, S.: BI+AS+NS-ThA4, 188; TF-WeM3, 135
Frechet, J.M.J.: EM-WeM4, 122
Fréchet, J.M.J.: SS-ThP4, 220
Fredriksson, H.: NS+BI-MoM9, **8**
Freitag, B.: IS+AS-FrM7, **235**
Friebel, D.: IS+AS-ThA2, **193**
Friedman, A.L.: GR+EM+MS-TuM4, 51
Friesen, B.A.: NS+BI-MoM10, 8
Fuentes-Cabrera, M.: TF-WeM4, 136
Fuhrer, A.: MI+EM-WeA12, 151
Fuhrer, M.: GR+SS-MoA4, 27
Fuhrmann, B.: SE+TF-TuA7, 77; TF-ThP31, 229
Fujikawa, Y.: SS1-FrM4, 242
Fukasawa, M.: PS1-TuM9, 54
Fukuda, S.: PS2+MN-WeA3, 155; PS2-ThA2, 202
Fukuoka, T.: SE+TF-TuA4, 77
Fukutani, K.: AS-TuP25, 93
Fullerton, E.E.: MI+TF-ThA6, **194**
Funk, M.: PS2-ThA4, 202; PS2-ThM2, 179; PS2-ThM9, 180; PS-ThP17, 219
Funnemann, D.: AS-WeM2, 119
Fuqua, P.: TF2-MoA10, **39**
Furlani, E.: IJ+MN+TF-WeA7, 149
Furman, B.: NS+BI-MoM1, 7
Furuta, T.: SS-ThP12, **221**
Fuyuki, T.: PS-FrM10, 241

— G —

Gabriel, C.: PS2-ThA10, 203
Gaddam, S.: PS1-MoM3, 9
Gade, L.H.: SS2-ThA7, 206
Gai, Z.: MI+TF-ThA11, **195**; MI+TF-ThA4, 194
Gale, B.: BM+MN+MS+TF+BI-ThA6, 190
Gall, D.: SE+TF-TuA8, 77; TF2-MoA8, 38
Gallego, J.M.: MI-FrM5, 237; SS1-FrM2, 242; SS2-ThA10, 207; SS2-ThM10, 183
Galoppini, E.: SS2-TuA11, 81
Gaman, C.: PS2+PV-MoM11, 12; PS2-ThM4, 179
Gambin, V.: GR+AS-WeA3, 148
Gamble, L.J.: AS+NS-WeM9, 118; BI-ThP18, 212; BI-TuM5, **46**; BI-TuP13, 96; SS2-FrM6, 245
Gammon, D.: EM-ThA2, 191
Gandikota, S.: MS-ThA4, 197
Ganesh, N.: SE+TF-TuA1, 76
Gangopadhyay, A.K.: TF-WeM9, 136
Gann, R.D.: SS1-FrM9, **243**; SS1-TuM3, **58**
Gao, F.: AS-WeM11, 120; PS2+MN-WeA1, **154**; PS2+MN-WeA2, 154
Gao, G.T.: TR+NS-WeM5, 138
Gao, H.: NS-TuP17, **103**
Gao, H.J.: SS2-WeA8, 158
Gao, J.: IJ+MN+TF-WeA7, 149; NS-WeM4, 126
Gao, L.: NS+BI-MoA3, 28
Gao, S.: MN+IJ+TR-ThA8, 196
Gao, X.: AS+NS-WeM4, 117
García Flores, H.G.: SS1+AS+TF-ThM10, **182**
Garcia, H.: TF-WeM9, 136
Garcia, J.: SE-TuP6, 110; TR-ThP2, **231**
Garfunkel, E.: EM-TuA3, 69; EM-TuA4, 69; EM-TuA9, 70; GR-MoM4, 5
Garner, M.: EM-TuA7, 69
Garnica, M.: GR+AS-WeA7, 148; GR+TF-TuA4, 71
Garramone, J.J.: AS-WeM9, **120**; MI-ThP1, 214
Garrity, K.: SS1+EM-MoA4, 32
Gartsman, K.: TR+SS-TuA10, 87
Gaskill, D.K.: GR+EM+MS-TuM4, **51**; GR+SS-MoA3, 27; GR+TF-TuA3, 71
Gaspar, D.J.: AS-FrM6, **232**
Gassman, P.L.: SS1-FrM5, 242
Gates, S.M.: PS2+TF-WeM3, 130
Gatilova, L.: PS2-ThA8, 203
Gauntt, B.D.: AS+EM+MS+TF-MoM5, 2
Gawande, S.: IJ+MN+TF-WeA10, 149
Ge, S.: TR+SS-TuA11, 87
Ge, Y.: SS2-ThA11, 207
Gebhardt, C.: SS1+PS+TF+AS+NS-TuA12, 80
Geer, R.E.: MS-ThA1, **197**
Geil, R.D.: AS-FrM11, 233
Geisler, H.: GR+TF-TuA10, 72
Gellert, P.R.: IJ+BI+MN+SE+AS-ThM10, 169
Gellman, A.J.: NS+BI-MoM8, 8; SS2-TuM9, **61**; SS2-WeM1, 133
Genis, A.P.: VT-TuP11, 115
George, S.M.: TF2-MoM3, 20; TF2-TuA2, 84; TF2-TuA9, 85; TF3-MoA6, 39; TF-WeA8, 160; VT-WeM1, **139**
Gerbaux, P.: TF2-MoA2, 37
Gerber, R.W.: TF-ThM10, 185
Gerlach, J.W.: SE+TF-TuA7, 77
Germack, D.S.: AS+EM+MS+TF-MoM9, 3
Geron, T.: BI-ThP6, 210
Gerson, Y.: MN-FrM6, 238
Gessert, T.A.: TF1+PV-MoA10, 37; TF1+PV-MoA6, 36; TF1+PV-MoA8, **37**; TF-FrM5, 247; TF-ThA9, 208
Gherardi, N.: PS2-TuM3, **56**
GhezelAyagh, H.: SS1-FrM10, 244
Ghong, T.H.: AS-TuP2, 89
Ghosal, S.: AS+NS-TuA1, 67
Giangregorio, M.: BI+NS-MoM1, 4; SS2-TuA1, 80
Giannuzzi, L.A.: AS1-ThM5, **164**
Gibson, D.R.: TF-FrM9, 247
Gielis, J.J.H.: SS2-FrM2, 244
Giet, J.M.: PS-FrM2, 240
Gil, E.L.: PS2+PV-MoM2, 11; PS-TuP11, 107
Gil, J.: BI+AS+NS-WeA11, 145
Gila, B.: MI+EM-WeA4, 150; VT-TuP10, 115
Gillen, G.: AS1-ThM6, 164
Gillon, X.: AS+NS-TuA3, 67
Gilmer, G.: TF1-TuA10, 84
Gilmore, I.S.: AS1-ThM2, **164**
Gil-Rostra, J.: TF1-TuA7, 83
Ginger, D.S.: NS1+PV-TuA1, **72**
Ginley, D.S.: AS-FrM6, 232; TF-WeA2, 159
Giors, S.: VT-WeM9, **140**
Glaser, E.: GR+SS-MoA3, 27
Gleason, K.: TF2-TuM3, **64**; TF-WeA10, 160
Glotzer, S.C.: BP+NS-SuA3, **1**
Glukhoy, Y.: SE-MoA7, **31**
Goeckner, M.: PS2-TuM11, 57; PS-TuA3, **75**
Goel, N.: EM-TuA1, 69; EM-TuA7, 69; NS+BI-MoA3, 28
Gogte, Y.: MN-FrM9, 239
Gokce, B.: SS2-FrM1, 244
Goldhahn, R.: AS+EM+MS+TF-TuM6, 44
Goldsmith, C.L.: IJ+BI+MN+SE+AS-ThM5, 169
Gölzhäuser, A.: GR-MoM9, **6**; SS2-ThM12, 184
Gomeniyuk, Y.: TF-ThP23, 227
Gonon, P.: TF2-MoA9, 38
Gonzalez, E.: SE-MoA4, **31**
Gonzalez-Elipe, A.R.: SE+TF-TuA10, 78; TF1-TuA7, 83
Gooding, T.: VT-MoA9, 41
Goodrich, T.L.: VT-TuP5, 114
Goorsky, M.: NS+BI-MoA3, 28
Goossens, V.: TF2-MoA2, 37
Gorai, P.: MS-ThA3, 197; SS2-FrM10, **246**
Gorb, L.G.: SS1+AS+TF-ThM4, **181**
Gordon, M.: AS+NS-TuA2, 67; NS-ThM10, **176**; NS-ThM2, 175
Gordon, R.G.: TF2-MoM10, 21; TF2-MoM4, **20**
Gordon, R.J.: AS-TuP5, 89
Gorham, J.: SS1+PS+TF+AS+NS-TuA1, 78
Görlitz, D.: MI+TF-ThA9, 195
Gorman, B.P.: AS1-ThM5, 164; NS-ThA3, 198
Gorodetsky, A.: BI+AS+NS-FrM3, 234; NS1+PV-TuA10, 73
Goryl, M.: NS-TuP29, 104
Goto, M.: MN-ThP2, 215
Goto, T.: PS2-ThM12, **181**
Gottfried, J.M.: SS2-WeM6, 134
Gougousi, T.: TF2-TuA3, **85**
Gouraud, P.: PS1-TuM5, 54
Gourvest, E.: AS+EM+MS+TF-TuM5, **43**
Grabow, L.: SS3-TuA3, 81
Grace, J.M.: IJ+MN+TF-WeA11, **149**; IJ+MN+TF-WeA7, **149**
Graciani, J.: SS1-TuM9, 59; SS3-TuA1, 81
Graham, J.F.: NS2-TuA3, **74**
Graham, M.E.: SE1-MoM3, 12
Grainger, D.W.: BI+AS+NS-ThA9, 189; BI-ThP13, 211
Grandjean, N.: EM-ThA3, **191**
Granozzi, G.: GR-MoM4, 5
Grass, M.: IS+AS-ThA9, 194; IS+SS-ThM2, **170**; SS2-MoA11, 35
Grassian, V.: AS+NS-WeM1, **117**; SS1-WeM5, **132**
Graur, I.A.: VT-WeA1, **162**
Graves, D.B.: PS1-MoM4, 9; PS1-ThA9, 201; PS1-ThM1, **177**; PS-FrM3, 240; PS-TuA10, 76; PS-TuA12, 76; PS-TuA8, 75; PS-TuA9, 75
Gray, K.A.: SE1-MoM3, 12
Greczynski, G.: SE2-MoM3, 14; TR+SE-WeA1, 161
Green, F.: PS2-ThM4, 179
Green, F.M.: AS1-ThM2, 164
Greene, A.: BM+MN+MS+TF+BI-ThA3, 189
Greenwood, C.L.: PS-ThP9, 218
Grehl, T.: AS-FrM5, **232**
Greilich, A.: EM-ThA2, 191
Grest, G.S.: TF-ThA10, 208
Griesser, H.J.: PS-TuP17, 108
Grigoropoulos, C.P.: BI+AS+NS-FrM4, 234
Grill, A.: PS2+TF-WeM3, 130
Grimm, R.L.: SS2-ThM9, 183; SS-ThP16, 222
Groll, M.: BI+AS+BM+MS-WeM3, **121**
Grøndahl, L.: BI-TuP11, 95
Groner, M.D.: TF3-MoA6, 39

Gros, L.: MI+EM-WeA12, 151
Groß, A.: SS2-ThA9, 206
Gross, E.: SS3-TuA10, **83**; SS-TuP1, **111**
Groves, J.T.: BI+AS+NS-ThA1, **187**
Grundmeier, G.: SS2-TuA10, 81
Grunze, M.: BI-TuA8, 68
Grutter, P.: EM-ThA1, 191; MI-ThP3, 214; TF1-TuA11, 84
Gruverman, A.: BI+AS+NS-FrM6, 234
Gschwender, L.: SS1-WeA3, 156
Gu, G.D.: SS1-TuM3, 58
Gu, X.: NS-WeA4, **152**
Gudmundsson, J.T.: PS1-WeA8, **154**; TF1-MoM6, **19**
Guella, G.: BM-ThP4, 213
Guest, J.R.: GR-TuP4, 100
Guha, J.: PS+MS-MoA6, 30; PS1-ThA6, 200
Guilak, F.: BI-TuP10, 95
Guilet, S.: PS2-ThA8, 203
Guillermet, M.: PS1-MoM10, 10
Guisinger, N.P.: GR-TuP4, **100**
Gullapalli, S.K.: TF-WeA3, **159**
Gundlach, D.J.: AS+EM+MS+TF-MoM9, 3
Gundogdu, K.: SS2-FrM1, **244**
Guo, J.-H.: IS+AS-ThA1, **193**
Guo, Q.: SS1-FrM1, **242**
Gupta, A.: TF1-MoM3, **19**
Gupta, G.: BI-TuP2, 94
Gupta, S.: MI+TF-ThA8, 195
Gurney, B.A.: GR+MI-WeM2, 124; MI-ThM5, 172
Guschl, P.: SE-MoA4, 31
Gustafsson, T.: EM-TuA3, 69; EM-TuA4, 69; EM-TuA9, 70
Gutmann, S.: EM-TuP11, 97; SS1-TuM1, **58**
Guvenc, H.O.: BI-ThP11, 211
Gweon, G.H.: PS2-ThM5, 179; TF-ThP16, **226**
— H —
Haack, J.R.: AS-WeM12, 120
Hackley, J.C.: GR+EM+MS-TuM6, **51**
Hada, M.: AS-ThA8, 187
Haddon, R.C.: NS-WeA7, **152**
Hadjar, O.: AS-TuP33, **93**
Hagen, K.: SS1+PS+TF+AS+NS-TuA1, 78; SS1+PS+TF+AS+NS-TuA7, 79
Haggerty, N.: BI-ThP20, 213
Haglund, R.F.: TF-ThA2, 207; TF-ThA6, 207
Haider, B.: NS-WeM11, 127
Haile, S.: NS-ThM4, 176; TF1-TuA9, 84; TF-ThP37, 230
Hakanoglu, C.: SS1-TuM11, 59
Hall, R.: TF2-TuA9, 85
Ham, H.: SS2-MoA2, **34**; SS2-TuM12, 61
Hamada, I.: SS2-WeA2, 157; SS-TuP2, 111
Hamaguchi, S.: PS1-ThM10, 178; PS1-TuM9, 54
Hamers, R.J.: AS+NS-WeM12, 119; NS-WeM1, **126**; SS1-MoM8, 16; SS2-FrM5, 245; SS2-ThM4, 183
Hammond, J.S.: AS-ThA10, **187**; AS-ThA9, 187; EW-TuL4, **66**; NS-ThA2, 198
Hampel, P.: BI+AS+BM+MS-WeM11, 121
Hamza, A.V.: AS+NS-TuA1, 67; NS-WeM5, 126; TF2-TuM12, 65
Han, P.X.: AS+NS-TuA9, **68**
Han, S.M.: EM1+PV-TuM11, 48; EM-TuP5, 97
Han, W.: GR+MI-WeM6, **125**
Han, Y.: SS1-ThA3, **204**
Hanbicki, A.T.: MI+EM-WeA9, 151; MI-ThP5, **214**
Hanif, K.M.: MI+TF-ThA10, 195
Hanley, L.: AS-ThA6, **186**; AS-TuP5, 89
Hansen, T.A.R.: AS+EM+MS+TF-TuM9, 44; PS1-ThA3, **200**
Hansen, T.W.: SS1+PS+TF+AS+NS-TuA7, 79
Hanson, E.G.: IJ+MN+TF-WeA3, **149**
Hao, S.: TF1-TuA1, 83
Hara, T.: TF-ThP7, **224**
Harb, J.N.: BI-ThP2, 210
Hargrove, W.F.: PS2-TuM6, 56
Har-Lavan, R.: NS1+PV-TuA11, **73**
Harper, J.M.E.: TF-ThM9, 185
Harrell, L.E.: MN-FrM7, 239
Harries, J.R.: AS-TuP9, **90**
Harris, K.D.: SE+TF-TuA9, 77
Harris, M.: EM-TuP21, 99
Harrison, J.A.: TR+NS-WeM5, **138**
Harrison, S.: PS-ThP2, **217**
Hartmann, N.O.: BI+AS+NS-ThA4, 188; TF-ThM4, 184; TF-WeM3, **135**
Haruyama, Y.: NS-TuP4, 101
Hashimoto, T.: EM-TuP7, 97
Haskel, D.: MI+TF-ThA10, 195
Hassanien, A.: EM-WeM3, 122
Hasselbrink, E.: BI+AS+NS-ThA4, 188
Hatake, D.: GR-MoM11, 6
Hatanpaa, T.: TF2-MoM1, 20
Hatta, S.: SS2-WeA2, 157; SS-TuP2, 111
Hauer, V.: VT-WeA3, 162
Havenstrite, K.: BI-MoA1, **25**
Hawkins, G.: IJ+MN+TF-WeA7, 149
Hayano, H.: AS-TuP14, 91
Hayashi, H.: PS1-MoM1, 9; PS-TuP7, 106
He, P.: AS+EM+MS+TF-MoM3, 2
Heald, S.: MI+EM-WeA3, 150
Healy, K.E.: BI+AS+NS-FrM4, 234
Hecq, M.: TF2-MoA2, 37
Hedgeland, H.J.: SS2-WeA1, 157; SS2-WeA12, 158
Hedgeman, K.: EM-TuP21, **99**
Hedrick, J.L.: TF-WeM2, 135
Heideman, W.: AS+NS-WeM12, 119
Heikkila, M.J.: TF2-MoM1, 20
Heile, A.: AS-TuP13, 91
Heilshorn, S.C.: BI-MoA6, 26; BM+MN+MS+TF+BI-ThA9, 190; NS2-TuA7, 74
Heinrich, H.: SS-TuP6, 112
Held, G.: BI-TuM4, **45**
Heller, E.J.: SS3-TuA9, 82
Heller, M.: VT-MoM5, **22**
Helmersson, U.: SE2-MoM6, 14
Hemminger, J.C.: EM1+PV-TuM3, 47; IS+SS-ThM3, **170**; SS1-WeM9, 132; SS2-ThM9, 183; SS-ThP16, 222
Henderson, M.A.: IS+SS-ThM6, 171; SS2-MoM9, 18
Hendricks, J.: VT-MoA9, **41**
Hendriksen, B.: EM-WeM4, 122
Henry, F.: PS2+TF-WeM10, **131**
Henry, Y.: MI+TF-ThA6, 194
Hensley, D.K.: TF-WeM4, 136
Henzie: NS+BI-MoA1, **28**
Heo, J.H.: NS-TuP10, 102; TF-ThP40, 230
Heo, W.: PS2+MN-WeA9, 155
Heremans, J.P.: EM1+PV-TuM1, **47**
Hermanns, F.: GR+TF-TuA4, 71
Herranz, M.A.: SS2-ThA10, 207
Herranz, T.: SS2-TuM1, 60
Herrera-Gómez, A.: EM-TuA8, 69
Herrmann, K.: MN+IJ+TR-ThA8, 196
Hersam, M.C.: GR+EM+MS-TuM11, 52; SS-TuP5, 112
Herzinger, C.M.: AS+EM+MS+TF-MoM8, 3
Heydt, M.: BI-TuA8, 68
Hickman, N.: MS-ThA8, 198; SE1-MoM9, 13; TF-ThP42, 230
Hickman, S.A.: MN-FrM7, 239; MN-ThP7, **216**
Hicks, R.: NS+BI-MoA3, 28; SE-MoA4, 31
Hidai, H.: BI+AS+NS-FrM4, 234
Highsmith, A.L.: MN-ThP9, 216
Hightower, A.: NS-ThM4, 176
Hilfiker, J.N.: AS+EM+MS+TF-MoM3, 2; AS+EM+MS+TF-TuM10, **44**
Hill, F.C.: SS1+AS+TF-ThM4, 181
Hill, R.T.: BI+AS+NS-WeA10, **145**; BI-ThP16, 212
Hilner, E.: SS1+EM-MoA7, 32
Hiltrop, J.: PS-TuP19, 109
Himmelhaus, M.: BI-ThP11, 211
Hinarejos, J.J.: GR+AS-WeA7, 148; GR+TF-TuA4, 71
Hinch, B.J.: SS2-TuM5, 60; VT-MoA4, **41**
Hingerl, K.: AS+EM+MS+TF-TuM2, **43**; SE-TuP7, 110
Hinkle, C.L.: SS1+EM-MoA1, **31**
Hino, H.: TF-ThP10, 225
Hintzen, H.T.: EM1+PV-TuM12, 48
Hinze, P.: SS2-ThM12, 184
Hipps, K.W.: NS+BI-MoM10, 8; SS-ThP9, **221**
Hirao, T.: PS2-ThM6, 180
Hirata, M.: VT-TuP16, 116; VT-WeM11, 140
Hirayama, H.: GR+EM+MS-TuM5, **51**
Hird, J.: TR+SS-TuA3, 87
Hirohata, K.: TF-FrM7, 247; TF-ThP12, **225**; TF-ThP9, 224
Hirschmugl, C.J.: SS2-MoM2, 17
Hitchcock, A.P.: BI-ThP4, **210**; BI-TuM6, 46
Hite, J.K.: GR+EM+MS-TuM4, 51; GR+TF-TuA3, 71
Hitzman, C.: AS-FrM1, **232**
Hjort, M.: SS1+EM-MoA7, **32**
Hla, S.-W.: EM-WeM2, 122; EM-WeM3, **122**; MI+EM-WeA8, 151; MI-FrM6, 237; SS2-ThA8, 206
Ho, W.: SS2-WeA8, 158; SS2-WeA9, 158
Hoang, J.: PS1-WeA4, 153; TF2-TuA11, **86**
Hoban, J.A.: PS1-WeM9, 129
Hodges, D.R.: TF-ThP21, **227**
Höfer, U.: SS2-FrM8, 245
Hoffbauer, M.A.: EM-ThA9, 192
Hoffmann, G.: MI-FrM4, **237**; SS2-ThA8, 206; SS-ThP10, 221; SS-ThP8, 221
Hofman, T.: AS-TuP20, 92; SE+TF-TuA11, 78
Hofmann, T.: AS+EM+MS+TF-MoA3, 24; AS+EM+MS+TF-MoM8, **3**; TF1+SE-TuM6, 62
Höglund, C.: TF1-MoM8, **19**
Hohman, J.N.: BI+NS-MoM2, **4**; EM-TuP26, 99
Hoissiau, L.: AS-TuP13, 91
Holbrook, R.D.: AS+NS-TuA7, **67**
Hollenstein, Ch.: PS2+PV-MoM9, 12
Holloway, P.H.: EM-WeM10, 123; TF-ThA2, 207
Holm, W.: IJ+MN+TF-WeA12, 150
Holmberg, M.: BI-TuA7, **68**
Holsclaw, B.: SS2-WeM1, **133**
Holub, M.A.: MI+EM-WeA9, 151; MI-ThP5, 214
Homenuke, M.: BI+AS+NS-ThA3, 187
Hone, J.: BI+AS+NS-FrM3, 234; MN+GR-ThM1, **173**
Hong, B.Y.: NS-TuP18, 103; NS-TuP8, 101; NS-TuP9, 101; TF-ThP20, 227
Hong, J.K.: NS-TuP10, **102**
Hong, S.: MN+GR-ThM3, 173; SS1-FrM3, 242
Hong, S.P.: PS2-ThM5, 179; PS-ThP4, **217**; TF-ThP16, 226
Hong, S.S.: VT-TuP6, 114
Honma, Y.: GR-MoM11, 6
Hook, A.L.: IJ+BI+MN+SE+AS-ThM9, **169**
Hook, D.A.: MN+IJ+TR-ThA3, **196**
Höök, F.: BI+AS+NS-WeA3, 144
Hook, J.A.: BM+MN+MS+TF+BI-ThA8, 190
Hooke, W.M.: PS2-TuM6, 56
Hopkins, M.: EW-WeL3, **141**
Hopwood, J.: PS2-TuM10, 57; PS2-TuM12, **57**
Horak, D.: PS1-MoM9, 10; PS-TuP3, 106
Hori, M.: PS-ThP11, 218; PS-TuP20, 109; PS-TuP7, 106
Horita, S.: PS-FrM10, 241
Horn, M.W.: AS+EM+MS+TF-MoM5, 2; TF1-MoM9, 19
Hoshi, Y.: SE1-MoM6, **13**
Hosobuchi, E.: TR+SS-TuA1, 86
Hoster, H.E.: SS2-ThA9, 206; SS2-ThM11, 184
Hou, X.: BI-TuA7, 68
Houle, F.A.: EM-WeA7, **146**
Houston, B.: MN-FrM4, 238
Howling, A.A.: PS2+PV-MoM9, **12**

Hrbek, J.: SS1-TuM9, 59; SS3-TuA1, 81
Hseuh, H.C.: VT-WeA10, 163; VT-WeA11, **163**
Hsiao, C.N.: EM-TuP1, 96; TF-ThP22, **227**; TF-ThP26, 228; TF-ThP30, 229
Hsieh, A.H.: PS-TuP12, **107**
Hsieh, F.C.: TF-ThP30, **229**
Hsieh, J.H.: SE-TuM10, **58**; SS-TuP19, 113
Hsing, H.C.: SE1-MoM5, 13
Hsiung, G.Y.: VT-TuP13, **115**; VT-WeA12, 163
Hsu, C.C.: PS-ThP18, 219; PS-TuP12, 107; PS-TuP13, 107; PS-TuP14, 108; SE-MoA8, **31**
Hsu, K.: GR+AS-WeA11, 149
Hsu, Y.W.: PS-TuP14, **108**; SE-MoA8, 31
Hsueh, H.P.: VT-WeA12, 163
Hu, J.-P.: VT-TuP2, **113**; VT-WeA10, 163
Hu, Q.: SS1-FrM5, **242**
Hu, W.: NS1+PV-TuA3, 72; NS-WeM4, **126**
Hu, X.: SS2-TuM6, **60**
Huan, Q.: SS2-WeA8, **158**
Huang, B.: MS+GR+MI-ThM3, **174**
Huang, B.C.: SS1-ThA11, 205
Huang, C.: NS-TuP31, 105; PS-FrM10, 241
Huang, J.: EM-TuA1, **69**
Huang, J.H.: SE-TuP3, 110
Huang, J.R.: PS-ThP19, 220
Huang, M.: SS1-MoM5, 16
Huang, P.: SS1-WeA12, **157**
Huber, T.H.T.: PS-FrM7, 240
Hubert, D.: IS+AS-FrM7, 235
Hucknall, A.: BI-ThP12, 211
Hudait, M.: NS+BI-MoA3, 28
Hudson, E.A.: PS2-ThA2, 202; PS2-ThM11, **180**; PS-TuA10, 76; PS-TuA9, 75
Huemann, S.: SS2-ThM3, 182
Huerta, L.: AS-TuP29, **93**; SE-TuP6, 110
Huffaker, D.: NS+BI-MoA3, 28
Hug, H.J.: SE-TuM4, 58
Hughes, K.J.: SS1-FrM3, 242; TF2-MoM11, **21**
Hughes, Z.: GR+SS-MoA7, 27
Hull, R.: NS2-TuA3, 74
Hultman, L.: AS-TuP19, 92; SE2-MoM3, 14; TF1-MoM8, 19; TF1-TuA4, 83; TR+SE-WeA1, 161
Hunault, P.: TF1+PV-MoA2, 35
Hunger, R.: SS2-ThM3, 182
Hupp, J.T.: TF3-MoA1, **39**
Hurd, K.B.: BI-ThP2, 210
Husale, S.: BI+AS+BM+MS-WeM12, 121
Hussain, Z.: IS+AS-ThA9, 194
Hussein, R.O.: SE-MoA6, **31**
Hussein, Z.: IS+SS-ThM2, 170
Hutton, S.J.: AS-ThA1, **186**
Hwang, C.: GR-MoM3, 5; GR-TuP3, 100
Hwang, D.J.: BI+AS+NS-FrM4, 234
Hwang, G.: SS2-MoA2, 34; SS2-TuM12, 61
Hwang, J.: AS2+BI-ThM10, 167; TF-ThA2, 207
Hwang, S.Y.: AS-TuP3, 89
Hwangbo, C.K.: SE-TuP1, 109; SE-TuP2, 110
Hyde, L.D.: PS-TuP17, **108**

— I —

Iancu, V.: MI+EM-WeA8, 151; MI-FrM6, 237
Ichii, T.: AS-TuP16, **91**; AS-TuP4, 89; NS-TuP13, 102
Ichiki, K.: AS-ThA8, 187
Ichinohe, T.: TF-ThP10, **225**
Idzerda, Y.U.: MI+TF-ThA3, 194
Igarashi, M.: PS-FrM10, **241**
Ignatov, A.: NS-ThA1, 198
Iida, S.: AS-ThA9, 187
Ikebukuro, S.: AS-TuP15, **91**; AS-TuP16, 91
Ikeda, K.: AS-TuP8, 90; VT-WeM4, 139
Ikenaga, E.: AS-WeA11, 143
Ilavsky, J.: AS+NS-TuA1, 67
Ilic, B.R.: MN-FrM4, 238; MN-FrM5, **238**; MN-FrM8, 239
Illiberi, A.: PS1-ThM5, 177; TF-ThA8, **208**
Im, W.S.: AS1-ThM12, 165
Imai, Y.: SE+TF-TuA4, 77
Imamura, T.: PS1-MoM1, 9
Ingason, A.S.: TF1-MoM6, 19
Inglebert, R.: PS1-MoM10, 10
Inokuchi, A.: EM2-TuM11, 50
Inoue, F.: PS2+MN-WeA4, 155
Inoue, K.: NS-WeA10, 152
Isabell, T.C.: IS+AS-FrM3, **235**
Ishibashi, K.: PS2-ThM9, 180; PS-ThP17, 219
Ishihara, D.: SE1-MoM6, 13
Ishihara, K.: TF-FrM8, 247
Ismail-Beigi, S.: SS1+EM-MoA4, 32
Isnard, L.J.: VT-WeA2, **162**
Isobe, T.: SS-ThP12, 221
Isono, T.: BI-TuP8, **95**
Israel, A.: EW-TuA6, 70
Ista, L.K.: BI-TuP3, 94
Itakura, Y.: AS-TuP25, **93**
Ithaca, J.: VT-MoA2, 40
Ito, N.: TF-FrM2, 246; TF-ThP27, 228; TF-ThP6, 224
Ito, T.: PS1-ThM10, 178; PS1-TuM9, **54**
Itoh, H.: NS-TuP16, **103**
Iwabuchi, Y.: TF-ThP12, 225; TF-ThP9, 224
Iwai, H.: AS-WeA11, 143
Iwasaki, S.: NS-WeA10, 152
Iwasaki, Y.: GR-MoM11, 6
Iwashita, S.: PS2+TF-WeM5, **130**; PS-TuP21, 109

— J —

Jackson, G.S.: IS+AS-ThA9, 194
Jackson, M.: NS+BI-MoA3, 28
Jaffe, J.E.: TF1+PV-MoA4, 36
James, C.: BM+MN+MS+TF+BI-ThA3, 189
James, D.: PS2+MN-WeA1, 154
Jang, C.: GR+SS-MoA4, 27
Jang, S.: EM-WeM1, 121
Janjua, S.Z.: MI-FrM8, **237**; MI-ThP4, 214
Jankowski, A.F.: BI-TuP14, **96**
Jardine, A.P.: SS2-WeA1, 157; SS2-WeA12, **158**
Jariwala, B.: VT-TuP17, **116**
Järrendahl, K.: AS+EM+MS+TF-MoA11, **25**; AS-TuP19, 92
Jay, G.: BI-TuP10, 95
Jaye, C.: AS1-ThM11, 165; TR+SE-WeA11, **162**
Jazdzyk, M.: SS2-ThA6, 206
Jee, H.S.: NS-TuP20, 103
Jen, A.K.-Y.: EM-TuP26, 99; EM-WeM1, 121
Jen, H.: EM-ThM12, **169**
Jen, S.H.: TF2-TuA2, 84; TF-WeA8, **160**
Jenko, M.: NS-TuP12, 102
Jenks, C.J.: SS2-WeM11, 134
Jeon, D.: EM-WeA1, 145; EM-WeA10, 146
Jeon, H.J.: BI+AS+NS-FrM4, **234**
Jeon, H.T.: TF-ThP35, 229; TF-ThP36, 229
Jeon, J.: MN+IJ+TR-ThA9, 196
Jeon, M.H.: MI-ThP2, 214
Jernigan, G.G.: GR+EM+MS-TuM4, 51; GR+SS-MoA3, **27**; GR+TF-TuA3, 71
Jesse, S.: AS2+BI-ThM9, 166; EM2-TuM6, 49
Jhan, G.: SE1-MoM4, 13
Ji, H.: NS-TuP17, 103
Ji, Y.: SS2-WeA11, 158
Jiang, P.: IS+SS-ThM5, 171; SS3-TuA8, 82; SS-TuP8, **112**
Jiang, W.: EM2-TuM1, 48; NS-TuP32, 105; SS3-TuA11, 83; TF1+PV-MoA4, 36
Jiang, Y.J.: SS2-WeA9, **158**
Jie, D.: EM-WeA9, 146
Jing, D.: SS1-ThA3, 204
Jing, S.: BI-ThP8, 210
Jinnai, B.: PS2+MN-WeA3, 155; PS2-ThA2, **202**; PS2-ThM11, 180; PS-TuA11, 76
Joachim, C.: EM-WeA9, 146
Johnson, K.: IJ+MN+TF-WeA9, 149
Johnson, S.L.: TF-ThA2, 207
Johnston, J.: AS-TuP5, 89
Johnston, S.: EM-TuP6, **97**
Jones, J.: SE2-MoM10, 15
Jones, K.: EM-WeA2, 145
Jones, L.: AS+NS-TuA2, **67**
Jones, R.: TF2-TuM6, 64
Jonker, B.T.: MI+EM-WeA9, 151; MI-ThP5, 214
Jonsson, M.: BI+AS+NS-WeA3, **144**
Jönsson, P.: BI+AS+NS-WeA3, 144
Joo, J.: PS-ThP1, **216**; TF-ThP13, 225
Jordan-Sweet, J.L.: PS1-ThM11, 178
Jorel, C.: TF2-MoA9, 38
Joseph, E.A.: PS1-ThM11, 178; PS-TuA3, 75
Joubert, O.: PS1-MoM10, 10; PS1-MoM11, 10; PS1-MoM5, 9; PS1-ThA7, 200; PS1-TuM5, 54
Jousseaume, V.: TF2-MoA9, 38
Jung, C.R.: PS2+MN-WeA9, 155; TF-ThP44, 231
Jung, D.: BI-TuP6, 94
Jung, E.J.: AS1-ThM12, **165**
Jung, I.: GR+TF-TuA10, 72
Jung, I.S.: NS-TuP10, 102
Jung, J.: SS1-WeM3, 132
Jung, J.K.: PS-TuP2, 105
Jung, S.Y.: GR+MI-WeM12, 125; GR+MI-WeM5, **124**
Jung, T.A.: NS+BI-MoA6, 29; SS2-ThA1, 205; SS2-ThA7, 206
Jung, Y.C.: MN-ThP4, **215**
Jung, Y.S.: TF3-MoA6, 39
Jung, Y.W.: AS-TuP2, **89**
Jur, J.S.: TF2-MoM9, **21**

— K —

Kachian, J.S.: SS1-MoM1, **15**
Kage, R.: PS-TuP18, **108**
Kahn, E.: EM-ThM9, **168**
Kaiser, W.: BI+AS+BM+MS-WeM11, 121
Kaizu, M.: SS2-WeA2, 157; SS-TuP2, 111
Kalinin, S.V.: AS2+BI-ThM9, **166**; EM2-TuM6, 49
Käll, M.: NS+BI-MoM9, 8
Kalyanaraman, R.: TF-WeM9, **136**
Kalyanaraman, V.: SS-ThP5, **220**
Kam, H.: MN+IJ+TR-ThA9, 196
Kamada, H.: AS-TuP8, 90
Kamarthy, G.: PS+MS-MoA6, 30
Kameshima, Y.: SS-ThP12, 221
Kamimura, T.: NS-WeA10, 152
Kaminatsui, T.: PS-TuP7, 106
Kamiyama, T.: TF-ThP11, 225
Kampen, T.: SS-TuP7, 112
Kamto, A.: MN-FrM10, **239**
Kanakasabapathy, S.: MS-ThA6, **197**
Kanda, K.: NS-TuP4, 101
Kanda, M,: AS-TuP4, **89**
Kang, H.: AS2+BI-ThM10, 167
Kang, M.S.: EM1+PV-TuM4, 47
Kang, S.B.: VT-TuP15, 115
Kang, S.-G.: TF1-TuA1, 83
Kang, S.K.: MI-ThP2, **214**; PS1-TuM4, 53; PS-TuP6, 106
Kang, S.W.: VT-TuP6, 114
Kang, Y.: NS-TuP4, **101**
Kang, Y.J.: AS-TuP3, 89
Kanisawa, K.: NS-ThA7, 199
Kanouff, M.: VT-WeM3, 139
Kao, J.S.: NS-TuP23, 104
Kao, P.: BI+AS+NS-WeA9, 145
Kaplan-Ashiri, I.: TR+SS-TuA10, **87**
Karabacak, T.: TF1+SE-TuM4, 62
Karabchevsky, A.: TF-ThP31, **229**
Karahashi, K.: PS1-ThM10, **178**; PS1-TuM9, 54
Karakoti, A.S.: AS+NS-WeM10, **118**; AS+NS-WeM11, 118
Karpusenka, A.: BM+MN+MS+TF+BI-ThA8, 190
Kasahara, A.: MN-ThP2, **215**
Kasai, H.: SS-TuP10, 112
Kasemo, B.H.: BI+AS+NS-WeA4, 144; NS+BI-MoM9, 8; SS2-MoA1, 33
Kaspar, T.C.: TF1+PV-MoA4, **36**
Katalinic, S.: SS2-TuA11, **81**
Katan, A.J.: EM-WeM4, 122
Katine, J.: MI+TF-ThA6, 194; MI-ThM5, 172
Kato, K.: PS-TuA11, 76; TF-ThP27, **228**
Kato, S.: AS-TuP14, 91; VT-TuP14, **115**
Kaufman, M.: NS-ThA3, 198

Kaufmann, S.: BI+AS+NS-ThA3, **187**; BI+AS+NS-ThA8, 188
Kaur, M.: AS+NS-WeM5, 117
Kawai, M.: SS1-TuM4, 58; SS1-WeM3, 132; SS2-WeM4, 134; SS-ThP13, 222
Kawakami, R.: GR+MI-WeM6, 125
Kawasaki, M.: IS+AS-FrM3, 235
Kawasaki, T.: TF-ThP10, 225
Kawase, Y.: TF-ThP12, 225
Kawashima, Y.: PS2+PV-MoM3, **11**
Kay, B.: SS1-WeA9, 156; SS-ThP7, 221
Kaya, S.: IS+SS-ThM11, **171**; SS1-WeM4, 132; SS3-TuA7, 82
Kayani, A.: NS-TuP32, 105
Kedzierski, J.: GR+SS-MoA6, 27
Kei, C.C.: TF-ThP30, 229
Keim, E.G.: AS-TuP11, **91**
Keim, N.C.: IJ+BI+MN-WeM1, **125**
Kelber, J.: PS1-MoM3, **9**
Kell, C.D.: NS2-TuA3, 74
Kelley, J.M.: SS1+AS+TF-ThM9, 182
Kellogg, G.: SS-ThP18, 222
Kemp, C.A.J.: AS-FrM3, 232
Kendall, B.R.F.: VT-MoM1, 21
Kendelewicz, T.: IS+SS-ThM11, 171; SS1-WeM4, 132
Kenney, J.A.: PS1-WeA3, 153; PS1-WeA7, **153**; PS-ThP5, 217
Keren, U.: MN-FrM6, 238
Kern, K.: SS2-ThA10, 207
Kerr, R.S.: TF3-MoA8, 40
Kessels, W.M.M.: AS+EM+MS+TF-MoA10, 25; PS2+PV-MoM8, 12; SS1+PS+TF+AS+NS-TuA8, 79; SS2-FrM2, 244; TF2-MoM5, 20; TF2-TuM11, 64; TF3-MoA7, **39**; TF-ThA8, 208
Keuning, W.: AS+EM+MS+TF-MoA10, 25; TF2-TuM11, **64**
Keville, B.J.: PS2-ThA9, **203**; PS-ThP15, 219
Khajetoorians, A.: SS1-ThA2, 204; SS2-TuM2, 60
Khan, R.: BI-ThP3, 210
Khare, C.: SE+TF-TuA7, **77**; TF-ThP31, 229
Khare, R.: PS2-ThM10, 180
Kholod, Y.I.: SS1+AS+TF-ThM4, 181
Khoury, C.G.: NS-WeM9, 127
Kibelka, G.: AS-TuP33, 93
Kienzle, D.M.: SS1-WeA10, 156
Kiihamäki, J.: PS2+MN-WeA1, 154; PS2+MN-WeA2, 154
Kikuchi, M.: SE1-MoM8, 13
Kim, B.I.: SS1-WeM1, **131**
Kim, C.: EM-WeA10, **146**
Kim, C.Y.: AS1-ThM12, 165
Kim, C.-Y.: IS+AS-FrM1, 235
Kim, D.: EM-ThA2, 191
Kim, D.-H.: EM-TuP18, 98
Kim, D.J.: EM-TuP23, **99**
Kim, D.O.: TF-ThP35, 229
Kim, E.J.: SS1-WeM1, 131
Kim, G.: MN-ThP5, 215
Kim, G.H.: NS-TuP20, **103**; NS-TuP22, 104; PS1-WeA11, 154; PS-TuP15, 108
Kim, H.: SS1-MoM8, 16; SS-ThP1, **220**; SS-ThP2, 220; TF-ThP44, 231
Kim, H.C.: TF2-TuA10, 86; TF-ThP36, 229
Kim, H.G.: TF-ThP36, 229
Kim, H.J.: AS-TuP2, 89; AS-TuP3, 89; NS-TuP8, 101
Kim, H.S.: PS-TuP2, 105
Kim, H.-Y.: EM-ThA10, 192; SS2-TuA2, **80**
Kim, I.: GR-TuP3, 100
Kim, I.K.: TF-ThP28, 228
Kim, J.: EM-ThA10, 192; EM-TuA10, 70; MN-ThP5, **215**; NS-TuP20, 103; SS2-TuA2, 80; SS2-TuM2, **60**; TF2-TuA10, 86
Kim, J.D.: SS1-ThA2, **204**
Kim, J.H.: EM-TuP15, **98**
Kim, J.-H.: PS1-WeM10, **129**
Kim, J.J.: SE-TuP1, 109
Kim, J.S.: PS2+MN-WeA9, 155; PS-TuP4, 106
Kim, K.H.: NS-TuP10, 102; NS-TuP7, 101; TF-ThP38, **230**; TF-ThP39, 230; TF-ThP40, 230
Kim, K.N.: PS2-ThM5, 179; PS-ThP4, 217
Kim, K.S.: BI-TuP6, 94
Kim, K.T.: NS-TuP20, 103; NS-TuP22, **104**
Kim, K.W.: NS-TuP8, **101**
Kim, M.: BI+NS-MoM2, 4; EM-TuP26, **99**
Kim, M.S.: TF-ThP35, 229
Kim, N.: EM-TuP22, **99**; EM-TuP8, 97; TF-ThP29, 228; TF-ThP4, 223
Kim, R.H.: MS-ThA6, 197
Kim, S.: AS-TuP2, 89; BI+AS+NS-WeA11, 145; TF-ThP44, 231
Kim, S.G.: PS-TuP15, 108
Kim, S.M.: SE+TF-TuA1, 76
Kim, S.O.: NS-WeA12, 153
Kim, S.W.: NS-TuP19, 103; NS-TuP21, **103**
Kim, S.Y.: NS-TuP19, **103**; NS-TuP21, 103
Kim, T.: PS1-TuM10, 54
Kim, T.H.: BI+NS-MoM1, 4; NS-WeM9, 127; SS2-TuA1, 80
Kim, T.J.: AS-TuP3, 89
Kim, W.: EM-TuP18, 98; GR-TuP3, **100**; TF-ThP44, 231
Kim, Y.: EM-TuP18, 98; SS1-TuM4, 58; SS1-WeM3, 132; SS2-WeM4, 134
Kim, Y.B.: EM-WeA1, **145**
Kim, Y.C.: TF-ThP36, 229
Kim, Y.D.: AS-TuP2, 89; AS-TuP3, 89; MN+GR-ThM3, **173**
Kim, Y.H.: PS-ThP14, **219**
Kim, Y.J.: AS-TuP6, **90**; SS3-TuA11, 83
Kim, Y.-S.: SS-TuP11, 113
Kimes, W.A.: TF-ThP34, 229
Kimmel, G.A.: SS1-WeA9, **156**; SS2-MoM6, 18; SS2-MoM8, 18
Kimura, K.: SE+TF-TuA4, 77
Kimura, Y.: PS2-ThM6, 180
Kinder, R.: PS2+TF-WeM12, 131; SS1-FrM8, 243
King Liu, T.-J.: MN+IJ+TR-ThA9, 196
King, P.D.C.: EM-ThM3, 167
King, W.: NS+BI-MoM5, 8
Kingshott, P.: BI+AS+NS-FrM1, **234**
Kintaka, H.: PS1-TuM6, **54**
Kioseoglou, G.: MI-ThP5, 214
Kioussis, D.: AS+EM+MS+TF-TuM12, 45
Kipman, Y.: IJ+MN+TF-WeA9, 149
Kirk, W.P.: SS1-MoM5, 16; SS1-MoM6, 16; VT-WeM3, **139**
Kirkpatrick, E.M.: SE-TuP5, 110
Kirkpatrick, S.R.: SE-TuP5, 110
Kirsch, P.D.: EM-TuA1, 69
Kishimoto, T.: NS-WeA10, 152
Kitajima, T.: PS-TuP18, 108; SS1-FrM7, **243**
Kitano, M.: VT-WeM4, 139
Kiyokami, H.: PS1-ThM9, 178
Kizilkaya, O.: BI+AS+NS-FrM6, 234
Kjerstad, A.: AS+EM+MS+TF-MoA3, 24; AS-TuP20, **92**; SE+TF-TuA11, 78
Klein, T.M.: SS-ThP3, 220
Klick, M.: PS2+PV-MoM4, 11; PS-ThP3, **217**
Klimov, N.N.: GR+MI-WeM5, 124
Klimov, V.I.: EN-WeA1, **147**
Kline, J.S.: NS-ThA3, 198
Klingebiel, B.: TF-ThM4, 184
Klymko, N.: AS+EM+MS+TF-TuM12, 45; TF-WeA7, 159
Knezevic, J.: BI+AS+BM+MS-WeM11, 121
Knobloch, A.: MN+IJ+TR-ThA10, 197
Knoebel, J.L.: BI-ThP2, 210
Knoll, A.W.: TF-WeM2, **135**
Knoops, H.C.M.: AS+EM+MS+TF-MoA10, 25
Knorr, D.B.: EM-WeM1, **121**; NS-ThM3, 175; NS-WeA4, 152; TR+NS-WeM10, 138
Ko, A.: MS-ThA6, 197
Ko, C.: SS1-TuM5, 59
Ko, D.-H.: AS1-ThM12, 165; EM-TuP24, 99; NS-TuP19, 103; NS-TuP21, 103
Ko, G.: EM-ThA10, **192**
Kobata, M.: AS-WeA11, 143
Kobayashi, K.: AS-WeA11, **143**
Kobayashi, M.: EM-TuA7, 69
Kobayashi, S.: PS1-TuM9, 54
Kober, M.: SS-TuP8, 112
Köber, M.: IS+SS-ThM5, 171; SS3-TuA8, 82
Kobiela, T.: SS2-TuM10, 61
Koch, J.: TF-WeM3, 135
Kocherlakota, L.S.: NS-ThM3, **175**
Kockmann, D.: EM-WeM5, **122**
Kodama, M.: AS-WeA11, 143
Kodambaka, S.: GR+AS-WeA3, **148**; NS+BI-MoA3, 28
Koeble, J.: EM-WeA9, **146**; NS-ThA6, 199
Koehler, S.P.: SS2-WeA11, 158
Koel, B.: IS+SS-ThM1, **170**
Koenders, L.: MN+IJ+TR-ThA8, 196
Koga, K.: PS2+PV-MoM3, 11; PS2+TF-WeM5, 130; PS-TuP20, 109; PS-TuP21, 109
Koh, S.: SS3-TuA7, 82
Koh, S.J.: BI+NS-MoM6, 4; NS+BI-MoM11, 9; NS-WeM12, **127**
Koike, T.: EM2-TuM11, 50
Kolari, K.: PS2+MN-WeA1, 154
Komesu, T.: MI-ThM6, 173
Komissar, A.: NS-ThA1, 198
Komiyama, K.: TF-ThP14, 225
Kompa, K.: SS1+PS+TF+AS+NS-TuA12, 80
Konagai, M.: TF-ThP15, 226; TF-ThP5, 223
Kondo, M.: PS2+PV-MoM3, 11; PS2+PV-MoM5, 11
Kondo, T.: GR-MoM11, 6
Kondratenko, Y.: MS-ThA3, 197; SS2-FrM10, 246
Kong, J.: MS+GR+MI-ThM9, **175**
Koo, J.: SS2-FrM3, 244
Koops, R.: PS-FrM5, 240; VT-MoM4, 22
Koratkar, N.A.: TF1+SE-TuM1, **61**
Korchev, Y.E.: AS2+BI-ThM1, 165
Korenaga, Y.: PS-TuP20, 109
Korolkov, V.: BI-ThP20, **213**
Koster, N.B.: PS-FrM5, **240**; VT-MoM4, **22**
Kothnur, P.: PS2+TF-WeM12, **131**; SS1-FrM8, 243
Kotru, S.: EM-TuP16, 98; MN-ThP9, 216
Kotsubo, H.: TF-ThP12, 225; TF-ThP9, 224
Kotula, P.G.: TR+SE-WeA10, 162
Kouvetakis, J.: AS-TuP32, 93
Kover, L.: AS-WeM4, **119**
Kowalewski, T.: EM-WeM6, 122
Koyama, K.: PS-TuA11, **76**
Kozarsky, E.: NS-TuP20, 103
Kozioziemski, B.J.: AS+NS-TuA1, 67
Kramer, D.: NS-WeM5, 126
Kratzer, M.C.: SS-TuP13, **113**
Krause, K.M.: TF1+SE-TuM12, **63**
Kriele, A.: TF2-TuM12, 65
Krim, J.: MN+IJ+TR-ThA3, 196; TR+SE-WeA3, 161
Krishna, H.: TF-WeM9, 136
Kroemker, B.: AS-WeM2, 119
Krol, S.: NS-ThA1, 198
Kruger, M.B.: MI-FrM7, 237
Krupczak, E.: SS1+PS+TF+AS+NS-TuA11, 80
Krylov, S.L.: MN-FrM5, 238; MN-FrM6, **238**; MN-ThP6, 216
Kubala, N.G.: TF2-TuA4, **85**
Kubby, J.A.: IJ+BI+MN+SE+AS-ThM5, **169**
Kuboi, N.: PS1-TuM9, 54
Kucheyev, S.O.: TF2-TuM12, 65
Kuchibhatla, S.V.N.T.: AS+NS-WeM10, 118; AS+NS-WeM11, **118**; NS-TuP32, 105; SS1-FrM10, 244; SS3-TuA11, 83
Kuck, S.: MI-FrM4, 237; SS2-ThA8, **206**; SS-ThP10, 221; SS-ThP8, 221
Kudlacek, P.: PS1-ThM5, **177**
Kuehnle, A.: SS-TuP18, 113
Kuemin, C.: NS2-TuA1, 73
Künzel, D.: SS2-ThA9, 206

Kuk, Y.: GR+MI-WeM12, 125; NS-ThA8, 199; NS-TuP15, **102**
Kulik, H.J.: MI-FrM6, 237
Kulp III, J.: BI-TuM3, 45
Kumagai, T.: SS2-WeA2, **157**; SS-TuP2, **111**
Kumar, A.: AS+NS-WeM10, 118
Kumar, K.: BI+AS+NS-ThA8, **188**
Kumar, N.: TF-WeA11, 160
Kummel, A.C.: EM-TuP13, 98; EM-TuP17, 98; SS1+EM-MoA10, 33; SS1+EM-MoA3, 32; SS1+EM-MoA6, 32; SS2-WeM2, 133
Kung, S.C.: EM1+PV-TuM3, 47
Kunikata, S.: SS-TuP10, 112
Kunnen, E.: PS-TuA7, **75**
Kunze, A.: BI+AS+NS-WeA4, **144**
Kuo, H.: EM-ThM12, 169
Kuo, S.Y.: TF-ThP26, 228
Kurihara, K.: PS1-MoM1, **9**
Kurland, A.R.: AS+NS-TuA9, 68
Kurtz, R.L.: SS2-MoM10, **18**
Kurtz, S.: MS-ThA8, 198
Kushner, M.J.: PS1-MoM6, 10; PS1-ThM2, 177; PS2-ThM3, 179; PS-FrM1, 239
Kuz'min, V.E.: SS1+AS+TF-ThM4, 181
Kwak, J.: SS1-TuM6, 59
Kwon, B.S.: PS2+MN-WeA9, **155**
Kwon, H.C.: PS-TuP15, **108**
Kwon, J.M.: TF-ThP40, **230**
Kwon, J.W.: SE-TuP4, 110; TF-ThP25, **228**
Kwon, N.Y.: NS-TuP7, **101**
Kwon, S.-Y.: GR+AS-WeA3, 148
Kyoung, J.: EM-TuP20, 99
Kyslinger, M.: TF-ThP18, 226
Kyynäräinen, J.: PS2+MN-WeA2, 154

— L —

LaBella, M.: GR+SS-MoA10, 28; GR+SS-MoA7, 27
LaBella, V.P.: AS-WeM9, 120; MI-ThP1, 214
Labelle, C.: PS1-MoM9, 10; PS-TuP3, 106
Laboriante, I.: MN+IJ+TR-ThA4, 196; TR+SE-WeA4, **161**
Lacis, J.W.: TF2-TuA3, 85
Lad, R.J.: TF1+SE-TuM10, 63; TF1-MoM5, 19
Ladroue, J.: PS1-TuM12, **55**
Lahaye, D.: NS+BI-MoA7, 29
Lahr, D.L.: PS-TuP9, 107
Lai, F.I.: TF-ThP26, 228
Lake, R.E.: SS-ThP6, **220**
Lallo, J.: SS2-TuM5, 60
Lam, K.P.: BI-ThP4, 210
Lamarque, F.: TF-WeA9, 160
Lamb, R.N.: TF2-MoA6, 38
Land, D.P.: BI+AS+NS-WeA12, 145; BI-ThP14, 211
Landin, J.: AS+EM+MS+TF-MoA11, 25
Landis, E.C.: SS1-MoM8, 16; SS2-ThM4, **183**
Lang, J.C.: MI+TF-ThA10, 195
Lange, C.: PS1-WeM2, **128**
Lange, M.: SE2-MoM10, **15**
Langer, R.S.: BI-MoA3, 25; IJ+BI+MN+SE+AS-ThM9, 169
Langereis, E.: AS+EM+MS+TF-MoA10, **25**; TF2-MoM5, 20; TF2-TuM11, 64
Langford, S.: EM-ThM9, 168
Langhammer, C.M.: SS2-MoA1, 33
Lanzara, A.: GR+AS-WeA1, **147**
Lapointe, F.: GR+EM+MS-TuM3, 51; NS-WeA9, **152**
Laracuente, A.R.: EM-ThA2, 191
Larson, P.E.: NS-ThA2, 198
Larsson, E.M.: SS2-MoA1, 33
Laskin, J.: SS1-FrM5, 242
Latour, R.A.: BI-MoA10, 26; BI-TuM1, **45**; BI-TuP12, 95
Lau, C.N.: GR+EM+MS-TuM1, **50**; GR+MI-WeM6, 125
Lau, S.: SS1+PS+TF+AS+NS-TuA11, 80
Lauer, J.L.: EM-TuP19, 99; PS1-ThA10, **201**
Layet, J.M.: PS1-ThA1, 199
Lazic, P.: MI-FrM4, 237
Le Moal, S.: SS1-TuM10, 59
Le Tarte, L.: AS-TuP24, 93
Lea, A.S.: AS-FrM6, 232; AS-WeM12, **120**; SS1-FrM10, 244
LeClair, P.: MI+TF-ThA8, 195
Lee, B.: HI-MoM1, **6**; TF2-TuA10, 86
Lee, C.: PS1-TuM10, 54; PS-TuP1, 105
Lee, C.-T.: TF-ThP43, **231**
Lee, D.: NS-TuP25, 104
Lee, D.H.: NS-TuP18, **103**; NS-WeA12, **153**
Lee, D.-K.: EM-TuP24, 99
Lee, E.: SS2-WeA12, 158
Lee, E.Y.-M.: SS2-TuM5, 60
Lee, G.: SS2-FrM3, 244
Lee, G.S.: EM-TuP18, 98
Lee, G.Y.: TR+SS-TuA2, 86
Lee, H.: EM-TuP22, 99
Lee, H.C.: TF-ThP28, **228**
Lee, H.D.: EM-TuA3, 69; EM-TuA4, **69**; EM-TuA9, 70
Lee, H.R.: TF-ThP36, **229**
Lee, H.S.: NS-WeM6, 127; PS-ThP14, 219
Lee, J.: EM-TuA1, 69; MN+GR-ThM3, 173; NS-TuP25, 104; PS1-MoM4, **9**; PS-ThP1, 216
Lee, J.B.: PS2-TuM11, 57
Lee, J.H.: EM-TuP18, 98
Lee, J.L.S.: AS-ThA11, 187
Lee, J.R.I.: AS+NS-TuA1, 67; MI+TF-ThA10, **195**
Lee, J.S.: SS1+EM-MoA10, **33**; TF-ThP35, **229**; TF-ThP36, 229
Lee, J.W.: EM-TuP23, 99
Lee, J.Y.: PS1-TuM1, 53
Lee, K.H.: TF-ThP35, 229
Lee, M.: SS1-TuM12, **59**
Lee, M.L.: TF2-MoA1, 37
Lee, M.S.: PS-TuP2, **105**
Lee, N.-E.: EM-WeM11, 123; PS2+MN-WeA9, 155; PS-TuP4, **106**; PS-TuP5, **106**; TF-ThP44, 231
Lee, R.J.: AS+NS-WeM2, 117; AS-TuP10, 90
Lee, S.: BI+NS-MoM5, 4; EM-TuP13, 98; EM-TuP20, 99; SS1+EM-MoA6, 32
Lee, S.H.: PS1-WeA11, **154**; PS-TuP15, 108; TF3-MoA6, 39
Lee, S.K.: PS2+MN-WeA9, 155; PS-TuP2, 105
Lee, S.R.: MN+GR-ThM3, 173
Lee, S.U.: NS-TuP18, 103; TF-ThP20, **227**
Lee, T.G.: BI-ThP10, 211; BI-TuP6, 94
Lee, W: EM-TuP8, 97; TF-ThP29, **228**; TF-ThP4, 223
Lee, W.: SS2-FrM3, 244
Lee, W.J.: NS-WeA12, 153; PS-TuP2, 105
Lee, W.-K.: NS+BI-MoM5, 8
Lee, Y.J.: BI-ThP10, 211
Leedy, K.: AS-TuP21, 92
Lefaucheux, P.: PS1-TuM12, 55; PS2-TuM11, 57
Legare, J.: VT-MoM5, 22
Leggett, G.J.: AS2+BI-ThM3, **165**; BI-ThP9, 210
Lei, H.: SE1-MoM6, 13
Leick, N.: AS+EM+MS+TF-MoA10, 25; TF2-MoM5, **20**
Lejeune, M.: EM-TuP2, **96**; TF-WeA9, 160
Lemmo, A.V.: BI+AS+BM+MS-WeM5, 121
Le-Mogne, T.: TR-ThP1, **231**
Leonhardt, D.: EM1+PV-TuM11, **48**; EM-TuP5, 97
Leou, K.C.: PS-ThP19, 220
Lersch, T.: AS+NS-TuA4, 67
Leschkies, K.S.: EM1+PV-TuM4, 47
Leskela, M.A.: TF2-MoM1, **20**
Leszczynski, J.R.: SS1+AS+TF-ThM1, **181**; SS1+AS+TF-ThM4, 181
Leung, B.O.: BI-TuM6, **46**
Leung, K.T.: SS2-FrM7, **245**
Leusink, G.: EM2-TuM2, 49
Levesque, P.: GR+EM+MS-TuM3, **51**
Lévesque, P.L.: NS-WeA9, 152
Levi, D.H.: AS+EM+MS+TF-MoM1, 2; TF-FrM5, 247
Levine, P.D.: VT-MoA10, **41**
Levy, D.H.: TF3-MoA8, **40**
Levy, N.: SS-ThP4, 220
Lewis, A.: EW-TuA6, 70; NS-ThA1, **198**
Lewis, D.: EW-TuA6, 70; NS-ThA1, 198
Lewis, T.L.: SS1-WeM9, **132**
Leyte-Vidal, A.: MS-ThA8, **198**
Lhostis, S.: AS+EM+MS+TF-TuM5, 43
Li, C.: SE-TuM10, 58
Li, C.H.: MI+EM-WeA9, 151
Li, D.H.: EM-TuP18, **98**
Li, F.: TF1+PV-MoA2, **35**
Li, G.: TR+SE-WeA4, 161
Li, H: MI+TF-ThA3, 194
Li, H.: SS-ThP1, 220; SS-ThP2, 220; TF2-TuA10, 86
Li, J.: AS+EM+MS+TF-MoA6, 24; AS+EM+MS+TF-TuM11, 44; BM-ThP1, 213; EW-TuA5, **70**; TF1+PV-MoA6, 36
Li, J.H.: TF2-TuA10, 86
Li, K.: SS-ThP3, **220**
Li, M.: PS-TuA10, 76; PS-TuA9, 75
Li, N.: SS-ThP3, 220
Li, S.: SE+TF-TuA4, 77
Li, X.: TF-FrM5, 247
Li, Y.: VT-WeA7, **163**
Li, Z.: IS+AS-FrM2, 235
Liang, B.: NS+BI-MoA3, 28
Liang, J.: EM-ThM10, 168; EM-ThM11, **168**; NS-TuP31, 105
Liang, M.W.: PS-ThP19, 220
Liang, T.: AS-TuP22, 92; BM-ThP1, **213**; NS+TR-TuM2, 52
Lichtenstein, L.: SS-ThP10, **221**
Licitra, Ch.: AS+EM+MS+TF-TuM5, 43; PS1-MoM5, 9
Liedberg, B.G.: BI-TuA1, **68**
Lifka, H.: TF2-TuM11, 64
Lim, C.: EM-TuP8, **97**; TF-ThP4, 223
Lim, J.H.: PS2-ThM5, **179**; PS-ThP4, 217; TF-ThP16, 226
Lim, J.T.: SE-TuP4, **110**; TF-ThP25, 228
Lim, J.Y.: VT-TuP15, **115**; VT-TuP6, 114
Lim, S.: GR-MoM3, 5
Lim, S.-F.: BM+MN+MS+TF+BI-ThA8, 190
Lim, S.K.: PS-TuP15, 108
Lim, W.S.: PS1-TuM4, 53; PS-TuP6, 106
Lin, C.-H.: PS-ThP7, 217
Lin, H.-C.: EM-ThA6, 191
Lin, J.: SE2-MoM4, 14
Lin, S.C.: EM-TuP9, 97
Lin, T.: PS-TuA12, 76; SE1-MoM4, 13
Lin, W.T.: TF-ThP26, **228**
Lin, Y.: PS-TuP13, **107**; SE-MoA8, 31; TF2-MoM4, 20
Lin, Y.H.: NS-TuP26, 104
Lin, Y.W.: SE-TuP3, **110**; TF-ThP22, 227; TF-ThP43, 231
Linford, M.R.: BI-ThP2, 210; MN+GR-ThM5, 174; SS2-FrM4, **244**; TF2-MoA1, 37; TF2-TuM5, **64**; TF-WeM11, 136
Ling, C.: TF1-TuA1, 83
Linic, S.: SS2-MoA3, 34
Linnane, S.: PS2+PV-MoM11, 12
Linne, M.A.: IS+AS-ThA9, 194
Lins, U.: BI-ThP4, 210
Liou, B.H.: TF-ThP43, 231
Lipinsky, F.: AS-TuP13, 91
Lisboa, P.: AS2+BI-ThM6, **166**; BI+AS+NS-FrM5, 234
Lisowski, W.: AS-TuP11, 91
Liu, D.: TR+NS-WeM6, 138
Liu, D.-J.: SS2-WeM11, **134**
Liu, D.R.: EM-TuP3, **96**; TF-ThP30, 229
Liu, F.: BI-ThP13, **211**; MN+IJ+TR-ThA4, **196**; TF-WeA7, 159
Liu, F.C.: BI-ThP11, 211

Liu, G.: AS-TuP8, 90; IS+SS-ThM1, 170; MS-ThA4, 197
Liu, J.: AS+NS-WeM5, 117; BM+MN+MS+TF+BI-ThA6, 190; IS+AS-ThA8, 193; NS-ThM1, 175
Liu, L.-H.: GR+TF-TuA11, 72; GR-TuP2, **100**
Liu, P.C.: SE-TuM10, 58
Liu, P.J.: SS1-TuM9, 59; SS2-WeM3, 133; SS3-TuA1, 81; SS3-TuA4, 82
Liu, X.: AS+EM+MS+TF-MoM10, **3**; PS1-MoM8, 10; TF2-TuA10, 86
Liu, Y.: AS-TuP5, 89; SE+TF-TuA3, **77**
Liu, Y.K.: TF-ThP26, 228
Liu, Z.: AS-TuP8, 90; IS+AS-ThA9, 194; IS+SS-ThM2, 170; SS-ThP16, 222; SS-TuP8, 112
Livadaru, L.: NS-WeM11, 127
Lo, C.: TF-ThP19, **226**
Lobo-Checa, J.: SS2-ThA7, 206
Lock, E.H.: AS-FrM7, 233; AS-WeA8, 143; GR-MoM5, 5; GR-TuP1, 100; PS-TuA2, **75**
Loertscher, E.: NS2-TuA1, 73
Loginova, E.: GR+AS-WeA9, 148; GR+TF-TuA9, 72
Long, J.R.: MI-FrM3, 236
Longenecker, J.G.: MN-FrM7, **239**
Longo, C.: VT-WeA11, 163
Lopano, C.: AS+NS-WeM2, 117
Lopez, D.O.: MN+GR-ThM10, 174
Lopez, G.P.: BI-ThP9, 210; BI-TuP2, 94; BI-TuP3, 94; BI-TuP7, 94
Lopez-Lopez, M.: EM-TuA10, 70
Loscutoff, P.W.: SS1-MoM2, **15**; TF-ThP33, 229
Losego, M.: TF-ThM10, **185**
Losovyj, Ya.: EM-WeA11, 146
Losurdo, M.: BI+NS-MoM1, 4; NS-WeM9, 127; SS2-TuA1, **80**
Louie, M.: NS-ThM4, **176**
Louis, K.M.: AS+NS-WeM12, 119
Lovascio, S.: PS2-TuM2, 55
Lovejoy, T.C.: EM-ThM2, **167**; MI+EM-WeA3, 150
Lu, C.: EM-ThM10, 168
Lu, E.: MI+EM-WeA8, 151
Lu, P.: EM-WeM9, 123
Lu, T.Y.: SE1-MoM5, 13
Lucovsky, G.: EM2-TuM3, 49; EM2-TuM9, **49**; EM-TuA11, 70; PS1-ThM11, 178
Luere, O.: PS1-TuM5, 54
Lukanov, B.: SS1+EM-MoA4, 32
Lukaszew, R.A.: MI-ThM1, 172; SS1-ThA6, **204**
Lundgren, E.: SS1+EM-MoA7, 32
Lundin, D.: SE2-MoM6, **14**
Lunelli, L.: BM-ThP4, 213
Luo, J.: EM-WeM1, 121
Luo, M.: SS2-WeA7, 158
Luria, J.: NS1+PV-TuA10, **73**
Luxmi, L.: GR+SS-MoA6, 27
Lymberopoulos, D.: PS1-TuM1, 53
Lysenko, V.: TF-ThP23, 227
Lyubinetsky, I.: SS2-MoM8, **18**; SS2-WeM10, 134

— M —

Ma, H.: EM-TuP26, 99
Ma, K.: IJ+BI+MN+SE+AS-ThM11, 170
Ma, S.J.: SS3-TuA1, 81
Maboudian, R.: GR+SS-MoA11, 28; IS+AS-FrM10, 236; MN+IJ+TR-ThA4, 196; TR+SE-WeA4, 161
Macak, K.C.: AS-WeA7, 142
Machida, M.: AS-WeA11, 143
Mack, P.: AS-FrM7, **233**; AS-TuP1, 89; AS-WeA8, 143
Mackus, A.J.M.: AS+EM+MS+TF-MoA10, 25; SS1+PS+TF+AS+NS-TuA8, **79**
Madan, A.: AS+EM+MS+TF-TuM12, **45**; PS2+TF-WeM3, 130
Madani, A.S.: BI-ThP17, **212**
Madey, T.: SS1+PS+TF+AS+NS-TuA1, 78
Maechler, L.: PS2-TuM3, 56
Maeda, S.: PS-TuA11, 76
Maekawa, H.: SS-TuP10, 112
Magnus, F.: TF1-MoM6, 19
Magnuson, M.: AS-TuP19, 92
Magnusson, R.: AS-TuP17, **92**
Mahalingam, S.: EW-WeL5, **141**
Mähl, S.: SS-TuP7, 112
Maier, M.: AS-WeM2, **119**; EM-WeA9, 146; NS-ThA6, 199
Maier, S.: SS1-WeA11, 157; SS1-WeM12, **133**; SS2-WeM5, 134
Maitrejean, S.: AS+EM+MS+TF-TuM5, 43
Majhi, P.: EM-TuA1, 69
Makabe, T.: PS-TuP18, 108; SS1-FrM7, 243
Maksymovych, P.: EM2-TuM6, **49**
Manandhar, S.: PS1-MoM3, 9
Mancini, D.C.: MN+GR-ThM10, 174
Mandra, M.: PS2-TuM11, 57
Mangalam, A.S.: IJ+BI+MN+SE+AS-ThM5, 169
Mangham, A.N.: AS+NS-WeM12, 119
Mangin, S.: MI+TF-ThA6, 194
Manini, P.: VT-MoM9, **23**
Mankey, G.J.: VT-TuP12, 115
Marchelli, A.: PS-ThP16, 219
Marchesini, G.R.: BI+AS+NS-FrM5, **234**
Margarella, A.: SS-ThP16, 222
Margot, J.: PS2-ThA3, 202; PS-TuA1, 74
Maria, J.-P.: TF-ThM10, 185
Marinakos, S.: BI-TuP5, 94
Marinero, E.E.: GR+MI-WeM2, 124; MI-ThM5, 172
Markovic, N.: SS-TuP11, 113
Marks, L.D.: IS+AS-FrM9, 236; SS1-WeA10, 156
Marocchi, L.: BM-ThP4, 213
Marohn, J.A.: MN-FrM7, 239; MN-ThP7, 216; NS1+PV-TuA10, 73
Marquis, Jr., J.: AS+NS-TuA4, 67; AS+NS-WeM2, 117
Martel, R.: GR+EM+MS-TuM3, 51; NS-WeA9, 152
Mårtensson, G.E.: IJ+MN+TF-WeA12, **150**
Marti-Gastaldo, C.: MI-FrM5, 237
Martin, A.R.: PS2-TuM6, 56
Martin, F.: EM-WeM4, **122**; SS2-ThA10, 207
Martin, J.: TR+NS-WeM6, 138
Martin, J.M.: TR-ThP1, 231
Martin, M.: PS1-TuM5, 54
Martín, N.: SS2-ThA10, 207; SS2-ThM10, 183
Martin, S.: PS2+TF-WeM6, 130
Martinez-Tomas, C.: AS+EM+MS+TF-MoM1, 2
Maruyama, M.: BI+AS+BM+MS-WeM11, 121
Mary, C.: TR-ThP1, 231
Marzari, N.: MI-FrM6, 237
Masaki, S.: TF-ThP10, 225
Masel, R.: MN+IJ+TR-ThA10, 197
Maslar, J.E.: TF-ThP34, 229
Massines, F.: PS2-TuM3, 56
Mastro, M.A.: SS2-TuA2, 80
Mastrogiovanni, D.: EM-TuA3, 69; EM-TuA4, 69; EM-TuA9, 70; GR-MoM4, 5
Mastsuda, H.: AS-WeA11, 143
Mate, C.M.: TR+SE-WeA7, **161**
Matena, M.: SS2-ThA7, 206
Mathew, R.: TF-ThP19, 226
Mathias, P.: SE+TF-TuA1, 76
Mathieu, M.: BI+AS+NS-ThA4, **188**; TF-WeM3, 135
Matson, D.W.: AS-FrM6, 232
Matsui, S.: NS-TuP4, 101
Matsui, T.: PS2+PV-MoM5, 11
Matsumoto, K.: NS-WeA10, **152**
Matsumoto, M.: AS-TuP25, 93
Matsumoto, Y.: PS1-ThM10, 178
Matsuo, J.: AS-ThA8, **187**
Matsuoka, M.: SE1-MoM1, 12
Matsuoka, T.: PS2-ThM12, 181
Matsuzaki, H.: PS2+TF-WeM5, 130; PS-TuP20, 109
Mattei, S.: PS2-ThM10, 180
Mattevi, C.: GR-MoM4, **5**
Matthiesen, J.: SS1-WeA9, 156; SS-ThP7, **221**
Mauldin, C.: EM-WeM4, 122
Mavrikakis, M.: SS3-TuA3, 81
May, R.A.: AS+EM+MS+TF-MoA4, **24**
Mayer, C.: BI+AS+NS-ThA4, 188
Mayer, J.: SS2-ThM12, 184
Mayer, M.: BI+AS+NS-WeA7, **144**
Mayrhofer, P.H.: TF1-MoM10, **20**
Mazur, U.M.: NS+BI-MoM10, **8**
Mbenkum, B.: TF1+SE-TuM6, 62
Mbuga, F.: IS+SS-ThM11, 171
McArthur, S.L.: BM+MN+MS+TF+BI-ThA10, 190; BM+MN+MS+TF+BI-ThA4, 190
McCall, S.K.: MI+TF-ThA10, 195
McCandless, B.E.: TF1+PV-MoA7, 36
McCarty, K.F.: GR+AS-WeA9, 148; GR+TF-TuA9, **72**; IS+AS-ThA9, 194; SS2-TuM1, **60**
McClory, J.: EM-WeA11, 146
McClure, A.: MI+TF-ThA3, **194**
McClure, C.: TF1+PV-MoA1, 35
McConville, C.F.: EM-ThM3, 167
McCoustra, M.R.S.: SS1-WeA1, 155; SS1-WeA2, **156**
McCreary, K.: GR+MI-WeM6, 125
McCullough, R.D.: EM-WeM6, 122
McDaniel, A.H.: IS+AS-ThA9, 194
McDonald, P.: TF-ThP19, 226
McEuen, P.L.: GR+TF-TuA1, **71**
McFall, J.: SE1-MoM9, 13
McGaughey, A.: SS1-TuM12, 59
McHale, S.: EM-WeA11, **146**
McIntire, T.: SS2-ThM9, 183; SS-ThP16, **222**
McKendry, R.: AS2+BI-ThM4, 166
McKnight, T.E.: TF-ThM1, 184
McNenly, M.: TF1-TuA10, 84
McPeak, K.: TF2-MoA7, **38**
Meares, C.F.: BI+AS+NS-WeA12, 145
Medina, A.: SS1-FrM2, 242
Megahed, M.: SS1-FrM8, 243
Mehashi, K.: NS-WeA10, 152
Mei, Y.: BI-MoA3, 25
Mekaru, H.: MN-ThP1, **215**
Melechko, A.V.: TF-ThM1, 184; TF-WeM4, 136
Melitz, W.: EM-TuP17, 98; SS1+EM-MoA6, **32**
Melosh, N.: BI+AS+NS-ThA7, 188; BI-ThP19, 212
Mendez, S.: BI-TuP3, 94
Mendoza-Galvan, A.: AS-TuP19, **92**
Menendez, J.: AS-TuP32, 93
Meng, L.: PS1-WeM4, **128**
Menguelti, K.: PS1-TuM5, 54
Merche, D.: PS-FrM8, **241**
Meritan, A.: PS1-TuM12, 55
Merkle, A.: IS+AS-FrM9, 236
Methaapanon, R.: TF2-TuA7, **85**
Mette, G.: SS2-FrM8, **245**
Metz, A.: MS-ThA6, 197
Metzger, W.K.: EM-TuP9, 97; TF1+PV-MoA6, 36
Meulenberg, R.W.: MI+TF-ThA10, 195
Mewes, T.: MI+TF-ThA8, 195
Meyer III, H.M.: AS-FrM9, **233**; AS-WeM10, 120
Meyer, R.J.: SS2-MoA9, 34; SS2-TuM6, 60
Meyer, T.: SS2-ThM2, 182
Mezzacappa, A.: VT-TuP9, **114**
Michael, J.R.: TR+SE-WeA10, 162
Michels, J.J.: TF-FrM1, 246
Michna, T.: PS2-ThM4, 179; PS-ThP6, **217**
Midgley, A.: MI-FrM7, 237
Mignot, Y.: PS1-MoM8, 10
Miki, K,: AS-TuP16, 91
Mikkelsen, A.: SS1+EM-MoA7, 32; SS1+EM-MoA8, **32**
Milasinovic, S.: AS-TuP5, **89**
Milella, A.: PS2+TF-WeM6, **130**
Miles, A.: BM+MN+MS+TF+BI-ThA6, 190
Miller, B.P.: MN+IJ+TR-ThA3, 196
Miller, D.: PS1-ThM11, 178
Miller, D.J.: IS+AS-ThA2, 193; IS+SS-ThM12, **171**

Miller, G.: SS2-ThA6, 206
Miller, J.B.: SS2-TuM9, 61
Miller, L.: VT-MoA2, 40
Miller, N.: EM-ThA9, 192
Miller, S.: GR-MoM4, 5; MN+GR-ThM9, 174
Milojevic, M.: EM-TuA10, **70**; SS1+EM-MoA1, 31; TF2-TuA10, 86
Min, H.: BI-ThP10, **211**
Min, K.S.: PS1-TuM4, 53
Min, TH.: MI-ThP2, 214; PS1-TuM4, 53; PS-TuP6, **106**
Minami, T.: TF-ThP15, 226; TF-ThP5, 223
Mine, N.: PS2+TF-WeM1, 129
Minter, A.: SS1-TuM11, 59
Miotti, L.: EM2-TuM3, **49**; EM-TuA11, 70
Miranda, R.: GR+AS-WeA7, 148; GR+TF-TuA4, 71; MI-FrM5, 237; SS1-FrM2, 242; SS2-ThA10, 207; SS2-ThM10, 183
Mishima, R.: EM-WeM2, 122
Mishra, B.: SE2-MoM4, 14
Mishra, G.J.: AS-WeA7, **142**
Mishra, M.: TR+NS-WeM3, 137
Mittendorfer, G.: SE-TuP7, 110
Mitterer, C.: SE-TuM1, **57**
Miura, N.: PS2-TuM10, **57**
Miura, T.: TR+SS-TuA1, **86**
Miyahara, Y.: EM-ThA1, 191; MI-ThP3, 214
Miyamura, A.: EM-TuP7, 97
Miyata, H.: PS2+TF-WeM5, 130; PS-TuP21, 109
Miyata, T.: TF-ThP15, 226; TF-ThP5, 223
Mkhoyan, A.: GR-MoM4, 5
M'ndange-Pfupfu, A.: IS+AS-FrM9, **236**
Mo, C.C.: SE1-MoM5, 13
Mo, Y.: TR+NS-WeM3, 137
Mochiki, H.: PS2+MN-WeA4, **155**
Mock, J.J.: BI+AS+NS-WeA10, 145
Moenninghoff, T.: TR+NS-WeM1, 137
Moffitt, C.J.: TF1+PV-MoA3, 36
Mohney, S.E.: EM-WeA3, **146**
Momose, H.: PS-TuA11, 76
Montgomery, E.: TF1+SE-TuM6, **62**
Montiel, Z.: TF-ThP3, **223**
Montserrat, J.: TF-ThA11, 208
Moon, Ch.S.: PS-ThP11, **218**
Moon, D.W.: BI+AS+NS-WeA11, **145**; BI-ThP10, 211; BI-TuP6, 94
Moon, H.K.: TF-ThP44, **231**
Moon, J.: GR+EM+MS-TuM4, 51
Moon, J.Y.: PS-TuP2, 105
Moore, D.P.: SS1+AS+TF-ThM10, 182
Moore, E.F.: TF-ThP34, 229
Moore, J.: EW-WeL4, **141**
Moore, J.J.: SE2-MoM4, 14
Moors, M.: SS1-TuM10, **59**; SS2-TuM10, 61
Morad, J.: SS1-ThA9, 205
Morales, H.: EM-ThM5, **168**
Morales-Luckie, R.A.: AS-TuP29, 93
Morandotti, R.: PS-TuA1, 74
Moravej, M.: PS2-ThM11, 180
More, K.L.: AS-FrM9, 233; AS-WeM10, 120
Morf, P.: NS+BI-MoA6, 29
Morgan, C.G.: VT-MoM3, **22**
Mori, T.: PS1-TuM6, 54
Moriarty, T.: TF1+PV-MoA6, 36
Morikawa, Y.: SS2-WeA2, 157; SS-TuP2, 111
Morin, E.I.: BI+NS-MoM2, 4
Morton, S.A.: MI+EM-WeA11, 151
Moser, M.: TF1-MoM10, 20
Mostafa, S.: SS-TuP6, 112
Motobayashi, K.: SS1-WeM3, 132
Motyka, M.A.: AS+EM+MS+TF-MoM5, 2
Moulder, J.F.: AS-ThA10, 187; EW-TuL4, 66
Mraz, S.: SE-TuM3, 58
Mudiyanselage, K.: SS1-MoM10, **17**
Mueller-Sebert, W.: TF2-TuM12, 65
Müser, M.H.: NS+TR-TuM3, **52**
Muggeridge, M.: PS2+MN-WeA1, 154
Muhl, S.: TF-ThP3, 223
Mukherjee, S.: SE+TF-TuA8, **77**
Mulders, H.J.J.L.: SS1+PS+TF+AS+NS-TuA8, 79
Mullet, C.: SS1-ThA9, **205**
Mullins, C.B.: AS+EM+MS+TF-MoA4, 24; SS2-TuM3, **60**
Mun, B.S.: IS+SS-ThM2, 170; SS-TuP11, **113**
Mun, J.: GR-MoM3, **5**
Mundy, C.: SS1-WeA9, 156
Munoz Sanjose, V.: AS+EM+MS+TF-MoM1, 2
Munro, J.J.: PS-ThP2, 217
Muramoto, S.: AS-ThA3, **186**
Murase, K.: AS-TuP16, 91; AS-TuP4, 89; AS-TuP6, 90; NS-TuP13, 102
Murata, A.: SE1-MoM8, **13**
Muratore, C.: SE2-MoM10, 15
Muratov, E.N.: SS1+AS+TF-ThM4, 181
Music, D.: TF-ThM3, 184
Mustonen, O.: AS-TuP10, 90
Muto, Y.: TF-ThP12, 225; TF-ThP9, **224**
Mutus, J.: NS-WeM11, 127
Myers-Ward, R.L.: GR+EM+MS-TuM4, 51; GR+TF-TuA3, 71
Myneni, S.C.B.: IS+SS-ThM9, **171**
Mysak, E.: SS1-WeM4, 132

— N —

Na, J.-S.: TF2-MoM9, 21
Naboka, M.: SS-TuP18, 113
Nacci, Ch.: NS-ThA7, 199
Nachimuthu, P.: AS+NS-WeM11, 118; AS+NS-WeM5, 117; EM-WeM6, 122; IS+SS-ThM6, **171**; NS-TuP32, 105; SS2-MoM11, 18; SS3-TuA11, 83
Nachmias, T.: MN-FrM6, 238
Nadesalingam, M.P.: SS1-MoM5, 16; SS1-MoM6, **16**; VT-WeM3, 139
Nagaoka, T.: PS1-ThA8, 201
Nagase, M.: VT-WeM4, 139
Nagel, S.: IJ+BI+MN-WeM1, 125
Nahm, R.: TF-WeA12, **161**
Naitabdi, A.: NS-TuP14, 102; SS2-MoA10, 35
Nakajima, A.: AS-TuP7, 90; SS-ThP12, 221; SS-ThP14, 222; SS-ThP15, 222
Nakajima, K.: SE+TF-TuA4, 77
Nakamura, J.: GR-MoM11, **6**
Nakamura, K.: PS1-ThM9, **178**; PS-ThP10, **218**
Nakamura, S.: SE1-MoM8, 13
Nakanishi, H.: SS-TuP10, 112
Nakano, T.: PS-TuP18, 108; SS1-FrM7, 243
Nakasaki, Y.: PS1-MoM1, 9
Nakazaki, Y.: PS1-WeM1, **127**
Nam, S.-W.: TF-WeA1, 159
Nampoori, H.: MN-ThP9, 216
Nanayakkara, S.U.: AS+NS-TuA9, 68; NS1+PV-TuA4, **73**; NS-WeM10, 127; NS-WeM3, 126
Nandamuri, G.: GR+TF-TuA11, 72
Nandasiri, M.: NS-TuP32, **105**; SS3-TuA11, 83
Nanjo, S.: AS-TuP16, 91
Narita, S.: TF-ThP2, **223**
Nasim, F.: SS-TuP13, 113
Näslund, L.-Å.: IS+SS-ThM12, 171
Nason, S.: SE1-MoM9, **13**; TF-ThP42, 230
Natarajarathinam, A.: MI+TF-ThA8, 195
Naudé, N.: PS2-TuM3, 56
Nauka, K.: PS1-ThM6, 177
Nazarov, A.: TF-ThP23, 227
Ndieyira, J.: AS2+BI-ThM4, **166**
Ndione, P.F.: PS-TuA1, 74
Neal, J.R.: MI+EM-WeA11, 151
Nefedov, A.: SS-TuP18, **113**
Negri, R.E.: NS-ThA2, 198
Nel, A.E.: BP+NS-SuA5, **1**
Nelsen, E.: SS2-FrM4, 244
Nelson, C.T.: PS-TuA3, 75
Nelson, S.F.: TF3-MoA8, 40
Nelson, T.: EM-WeM6, 122
Nemanic, V.: VT-WeA4, **163**
Nest, D.G.: PS-TuA10, 76; PS-TuA12, 76; PS-TuA8, 75; PS-TuA9, 75
Neugebauer, J.: SS2-TuA10, 81
Neumann, M.J.: PS1-WeM4, 128; PS1-WeM9, 129; SE2-MoM11, 15
Newberg, J.: IS+SS-ThM11, 171; SS1-WeM4, **132**
Newell, D.B.: GR+MI-WeM5, 124
Newman, N.: TF1+PV-MoA10, 37
Ng, H.-T.: PS1-ThM6, 177
Ng, T.: BI-ThP14, **211**
Ngo, V.: MS-ThA7, **198**
Nguyen, H.: BI-ThP8, 210
Nguyen, T.Q.: SS-TuP10, **112**
Nicolella, D.: NS+BI-MoM1, 7
Nie, S.: GR+AS-WeA9, **148**; SS1-WeM11, 133
Nie, X.: SE-MoA6, 31
Nielsch, K.: MI+TF-ThA9, 195
Nigra, M.: NS+BI-MoM8, 8
Nikiforov, M.P.: AS2+BI-ThM9, 166
Nilsson, A.: IS+AS-ThA2, 193; IS+SS-ThM11, 171; IS+SS-ThM12, 171; SS1-WeM4, 132; SS3-TuA7, 82
Nimmrich, M.: SS-TuP18, 113
Ninomiya, S.: AS-ThA8, 187
Nishi, Y.: EM-TuA7, 69; EM-TuP19, 99; PS1-ThA10, 201; TF-FrM7, **247**; TF-ThP12, 225; TF-ThP9, 224
Nishioka, M.: GR+MI-WeM2, 124; MI-ThM5, **172**
Nishiwaki, M.: AS-TuP14, 91; VT-TuP14, 115
Nisol, B.: PS-TuP16, **108**
Nitin, N.: NS-WeA3, 152
Noguchi, T.: AS-TuP14, 91
Noh, T.H.: PS-TuP15, 108
Nohira, H.: AS-WeA11, 143
Nolph, C.A.: SS1+EM-MoA11, **33**
Nolting, F.: NS+BI-MoA6, 29
Nomoto, J.: TF-ThP15, **226**; TF-ThP5, 223
Nomura, T.: PS-TuP20, **109**
Nordlund, D.: EM2-TuM3, 49; EM-TuA11, 70
Norris, D.J.: EM1+PV-TuM4, 47
Northwood, D.O.: SE-MoA6, 31
Nothofer, H.-G.: NS+BI-MoA6, 29
Nottbohm, Ch.T.: SS2-ThM12, 184
Nozawa, T.: PS1-TuM6, 54; PS2-ThM9, 180; PS-ThP17, 219
Nsimama, P.D.: TF1-MoM2, 19
Ntwaeaborwa, O.M.: TF1-MoM2, **19**
Nuckolls, C.: BI+AS+NS-FrM3, 234; NS1+PV-TuA10, 73
Nunney, T.S.: AS+NS-WeM2, 117; AS-FrM9, 233; AS-TuP10, **90**; AS-WeM10, 120
Nurmi, J.T.: AS+NS-WeM5, 117
Nyce, G.: AS+NS-TuA1, 67

— O —

Obinata, M.: TF-ThP10, 225
Obloh, H.: TF2-TuM12, 65
Obst, M.: BI-ThP4, 210
Ocola, L.E.: MN+GR-ThM10, 174; NS2-TuA2, **74**
Oda, J.: TF-ThP5, **223**
O'Donnell, S.: GR-MoM8, 6
Oehrlein, G.S.: PS-TuA10, 76; PS-TuA12, 76; PS-TuA9, 75
O'Farrell, D.: PS2+PV-MoM11, **12**; PS2-ThM4, 179
Ogasawara, H.: IS+AS-ThA2, 193; IS+SS-ThM11, 171; IS+SS-ThM12, 171; SS3-TuA7, 82
Ogino, T.: BI-TuP8, 95
Ogitsu, T.: SS-ThP20, 223
O'Grady, C.P.: IS+AS-ThA2, 193
Oh, D.: SS1+PS+TF+AS+NS-TuA3, 79
Oh, H.: EM-TuP20, 99
Oh, J.: GR-MoM11, 6
Oh, J.S.: PS2+PV-MoM2, 11; PS-TuP11, **107**
Oh, T.-S.: TF-ThP37, **230**
O'Hara, N.: PS2-ThM4, 179
O'Hayre, R.: TF-WeA2, 159
Ohe, K.: AS-TuP16, 91
Ohfuchi, H.: AS-TuP8, 90
Ohiwa, T.: PS2+MN-WeA7, 155; PS-TuP7, 106
Ohlhausen, J.A.: AS-FrM10, **233**
Ohmi, T.: EM2-TuM11, 50; PS2-ThM12, 181; VT-WeM4, 139

Ohno, Y.: NS-WeA10, 152
Ohshima, M.: TF-ThP10, 225
Ohta, H.: NS+BI-MoA8, 29; PS1-ThA8, 201
Ohtake, H.: PS2+MN-WeA3, **155**; PS2-ThA2, 202
Ohuchi, F.S.: EM-ThM2, 167; MI+EM-WeA3, 150
Oila, A.: TR+NS-WeM9, 138
Ok, I.: EM-TuA1, 69
Oka, N.: SE1-MoM8, 13; TF-FrM2, **246**; TF-FrM7, 247; TF-FrM8, 247; TF-ThP11, 225; TF-ThP12, 225; TF-ThP24, 227; TF-ThP27, 228; TF-ThP6, 224; TF-ThP9, 224
Okada, K.: SS-ThP12, 221
Okada, M.: NS-TuP4, 101
Okada, T.: SS2-WeM4, 134
Okamoto, S.: PS2+MN-WeA4, 155
Okano, T.: AS-TuP25, 93
Okura, Y.: SE-TuM6, 58
Okuyama, H.: SS2-WeA2, 157; SS-TuP2, 111
Olafsson, S.: TF1-MoM6, 19
Olmstead, M.A.: EM-ThM2, 167; MI+EM-WeA3, 150
Olsen, B.G.: VT-TuP4, **114**
Olson, C.: MI-FrM7, 237
Olson, D.A.: VT-MoA9, 41
Oncins, G.: AS2+BI-ThM11, 167
Ong, J.C.: MN-ThP7, 216
Ono, K.: NS+BI-MoA8, 29; PS1-ThA8, 201; PS1-ThM9, 178
Ono, L.K.: SS2-MoA10, **35**; SS-TuP6, 112
Opdahl, A.: BI-TuP15, 96
Opila, R.L.: TF1+PV-MoA7, 36
Orihuela, B.: BI-TuA9, 68
Orje, J.: BI-MoA9, 26
Orlando, T.M.: SS1+PS+TF+AS+NS-TuA3, **79**
Orlicki, J.: BI-MoA8, 26
Ormrod, S.: VT-MoM11, **23**
Osabe, T.: MS-ThA6, 197
Osgood, R.M.: SS2-WeM9, 134
Oshima, M.: AS-TuP8, 90
Osminer, T.: MI-ThM2, 172
Ostendorf, A.: TF-WeM3, 135
Ostrovski, Y.: PS2+TF-WeM3, 130
Ostrovsky, A.: PS1-MoM10, 10
Ostrowski, S.G.: AS-TuP24, 93
Ostrowsky, A.: PS1-MoM5, 9
Osumi, K.: SS-TuP10, 112
Otero, R.: MI-FrM5, 237; SS1-FrM2, 242; SS2-ThA10, **207**; SS2-ThM10, 183
Otte, A.F.: NS-TuP15, 102
Ouk, T.: PS2-TuM9, 56
Ovchinnikov, O.: AS2+BI-ThM9, 166
Overney, R.M.: EM-WeM1, 121; NS-ThM3, 175; NS-WeA4, 152; TR+NS-WeM10, **138**
Overzet, L.J.: PS2-TuM11, 57; PS-TuA3, 75
Ozaydin-Ince, G.: TF-WeA10, 160
Ozkaya, D.: AS-FrM5, 232

— P —

Padmaperuma, A.B.: AS-FrM6, 232
Paesler, M.A.: PS1-ThM11, 178
Paffen, R.M.J.: PS2-TuM5, 56
Page, S.C.: AS-ThA1, 186
Pai, S.S.: NS-TuP26, 104
Paillet, M.: GR+EM+MS-TuM3, 51
Pakhomov, A.: MI+EM-WeA3, 150
Pakizeh, T.: NS+BI-MoM9, 8
Palacio, M.: MN-ThP3, **215**
Palekis, V.: TF-ThP21, 227
Palma, M.: BI+AS+NS-FrM3, **234**
Palmero, A.: TF1-TuA7, 83
Palumbo, F.: PS2+TF-WeM6, 130; TF-WeA10, 160
Pan, J.: BM+MN+MS+TF+BI-ThA8, 190
Pan, L.: TR+SE-WeA3, **161**
Panagopoulos, T.: PS1-TuM10, 54
Panetta, C.J.: TF2-MoA10, 39
Pankow, J.W.: TF1+PV-MoA3, 36
Papp, C.: AS-WeA9, 143
Pappas, D.: PS-FrM6, **240**
Pappas, D.P.: MI-ThM2, 172; NS-ThA3, 198
Paraschiv, V.: PS2-ThA11, 203
Pargon, E.: PS1-MoM10, 10; PS1-ThA7, 200; PS1-TuM5, 54
Parilla, P.: TF-WeA2, 159
Park: MI-ThM2, 172
Park, B.-G.: EM-TuP18, 98
Park, B.J.: MI-ThP2, 214; PS1-TuM4, **53**; PS-TuP6, 106
Park, C.D.: VT-MoM9, 23
Park, H.: TF2-MoM10, 21
Park, H.K.: TF-ThA6, **207**
Park, I.H.: EM-TuP18, 98
Park, J.: EM-TuP8, 97; TF-ThP4, **223**
Park, J.B.: PS1-TuM4, 53; PS2+PV-MoM2, **11**; PS-TuP11, 107; SS1-TuM9, 59; SS3-TuA1, 81
Park, J.S.: EM-WeM11, 123; PS2+MN-WeA9, 155
Park, J.W.: NS-TuP9, **101**
Park, J.Y.: AS-TuP22, 92; MI-ThP2, 214; NS-WeM6, **127**
Park, K.A.: VT-TuP6, 114
Park, S.H.: EM-TuP18, 98
Park, S.K.: PS-TuP2, 105
Park, S.S.N.: BI+AS+NS-WeA12, 145
Park, T.-H.: NS1+PV-TuA4, 73; NS-WeM10, 127; NS-WeM3, 126
Park, T.J.: TF2-TuA10, **86**
Park, T.Y.: TF-ThP35, 229
Park, Y.D.: MN+GR-ThM3, 173
Park, Y.J.: SE-TuP1, **109**; SE-TuP2, 110
Park, Y.R.: PS-TuP5, 106
Park, Y.S.: NS-TuP9, 101
Parkin, S.S.P.: MI-ThM3, **172**
Parlinska-Wojtan, M.: SE-TuM4, 58
Parpia, J.M.: MN-FrM4, 238; MN-FrM8, 239
Parsons, G.N.: TF2-MoM9, 21
Pascual, C.: BI+AS+NS-FrM5, 234
Pasquardini, L.: BM-ThP4, 213
Patel, S.: VT-TuP1, **113**
Patel, V.: PS2+TF-WeM3, 130
Paterson, A.: PS1-TuM10, **54**
Patscheider, J.: SE-TuM4, **58**
Patz, R.: PS1-MoM9, 10; PS-TuP3, 106
Patzig, C.: MI+TF-ThA9, 195; SE+TF-TuA7, 77; TF-ThP31, 229
Paul, D.F.: EW-TuL4, 66; NS-ThA2, 198
Peacock, N.T.: VT-MoM6, **22**
Pearce, R.: TF-WeM4, 136
Pearson, A.: NS2-TuA8, **74**
Pearton, S.J.: EM-ThA10, 192; MI+EM-WeA4, 150
Peden, C.: SS1-TuM6, **59**
Pedersen, A.: AS+NS-WeM12, **119**
Pederson, M.R.: MI-FrM3, 236
Pederzolli, C.: BM-ThP4, 213
Peeters, F.J.J.: PS2+PV-MoM8, 12; PS-TuP10, **107**
Pei, L.: MN+GR-ThM5, **174**
Pelissier, B.: AS+EM+MS+TF-TuM5, 43
Pélisson, A.: SE-TuM4, 58
Pelliccione, M.: GR+MI-WeM2, 124
Pender, J.: PS1-MoM9, 10; PS-TuP3, 106
Penner, R.M.: EM1+PV-TuM3, 47
Pereira-Medrano, A.G.: BM+MN+MS+TF+BI-ThA10, 190
Perera, U.G.E.: EM-WeM2, **122**; MI-FrM6, 237
Perez-Luna, V.: BI+NS-MoM5, 4
Perez-Murano, F.: TF-WeM12, 137
Periasamy, P.: TF-WeA2, **159**
Perng, Y.-C.: EM-ThA11, **192**
Perrine, K.A.: SS-TuP4, **111**
Perry, S.S.: TR+SS-TuA7, **87**
Persson, H.H.J.: BI+AS+BM+MS-WeM12, **121**
Peshek, T.J.: TF1+PV-MoA10, **37**; TF-FrM5, 247
Petcu, M.C.: EM1+PV-TuM12, **48**
Peterson, R.E.: AS+NS-WeM12, 119
Petit-Etienne, C.: PS1-ThA7, **200**
Petrik, N.G.: SS1-WeA9, 156; SS2-MoM6, **18**; SS2-MoM8, 18
Petronis, S.: BI+AS+NS-WeA3, 144
Petrosky, J.: EM-WeA11, 146
Petrov, I.: GR+AS-WeA3, 148
Petrova, V.: GR+AS-WeA3, 148
Petrovykh, D.Y.: AS-FrM7, 233; AS-WeA8, 143; BI-TuM3, 45; BI-TuP15, **96**
Petruzza, P.: PS-ThP16, 219
Pettersson, L.G.M.: IS+AS-ThA2, 193
Pham, D.-T.: SS2-ThM2, 182; SS2-ThM3, 182
Phaneuf, R.J.: PS-TuA12, 76
Phillips, J.D.: EM2-TuM10, 50; EM-TuP9, **97**
Phillips, M.A.: AS1-ThM2, 164
Phillpot, S.R.: NS+TR-TuM2, 52; TR+SS-TuA7, 87; TR+SS-TuA8, 87; TR+SS-TuA9, 87
Pi, K.: GR+MI-WeM6, 125
Pianetta, P.: EM-TuA7, 69
Piao, H.: AS-TuP24, 93
Piasecki, J.D.: AS+NS-TuA4, 67; AS+NS-WeM2, 117; AS-TuP10, 90; EW-WeM8, 124
Piens, M.: PS2+TF-WeM1, 129
Pierard, C.: PS-FrM2, 240
Piercy, P.: SS-ThP17, **222**
Pilet, N.: NS-ThM9, 176; TR+NS-WeM2, 137
Pimpinelli, A.: SS1-ThA4, 204
Piner, R.D.: GR+TF-TuA10, 72
Pines, E.: AS-FrM4, 232
Piotrowski, P.L.: TR+NS-WeM5, 138
Pipino, A.C.R.: PS2+PV-MoM8, 12
Pireaux, J.J.: AS+NS-TuA3, **67**; PS2+TF-WeM1, 129
Pires, D.: TF-WeM2, 135
Pirkle, A.: GR+AS-WeA10, **148**
Pisana, S.: GR+MI-WeM2, **124**
Pitchford, L.C.: PS2-TuM11, 57
Pitters, J.: NS-WeM11, **127**
Placencia, D.: NS1+PV-TuA12, **73**
Plach, T.: AS+EM+MS+TF-TuM2, 43; SE-TuP7, **110**
Plummer, E.W.: MI+TF-ThA11, 195
Pochas, C.M.: AS+NS-TuA9, 68
Podraza, N.J.: AS+EM+MS+TF-MoM5, **2**; AS+EM+MS+TF-MoM6, 2
Poelsema, B.: AS+EM+MS+TF-MoM11, 3; EM-WeM5, 122
Poenitzsch, V.Z.: NS+BI-MoM1, 7; NS-WeA3, **152**
Pohl, D.: SS-ThP17, 222
Pohl, K.: SS2-ThA6, 206
Poirier, J.-S.: PS2-ThA3, **202**; PS-TuA1, 74
Pokhodnya, K.I.: MI-FrM7, **237**; MI-ThP4, 214
Poleunis, C.: PS-FrM8, 241; PS-TuP16, 108
Polikarpov, A.: VT-WeA1, 162
Pollmann, J.: SS2-TuA7, **81**
Pollock, K.: PS-TuP19, **109**
Poole, P.: EM-ThA1, 191
Poon, H.C.: SS2-MoM2, 17
Pore, V.J.: TF2-MoM1, 20
Porsgaard, S.: IS+SS-ThM5, 171; SS1-WeM4, 132; SS3-TuA8, **82**; SS-TuP8, 112
Porter, L.M.: EM-WeM6, 122
Posseme, N.: PS1-MoM10, 10; PS1-MoM11, **10**; PS1-MoM5, 9
Postawa, Z.: AS1-ThM9, 165
Potapenko, D.V.: SS2-WeM9, **134**
Potma, E.O.: AS1-ThM3, **164**
Potrich, C.: BM-ThP4, 213
Pott, V.: MN+IJ+TR-ThA9, **196**
Poulsen, D.: SS-ThP4, 220
Pourmorad, F.: BI-ThP17, 212
Powell, C.J.: AS-WeA3, **142**
Pozuelo, M.: NS+BI-MoA3, 28
Prabhu, V.M.: AS+EM+MS+TF-MoM9, 3
Prasad, S.: NS-TuP32, 105
Prasad, S.V.: TR+SE-WeA10, 162
Prégent, J.: PS-FrM9, **241**
Premkumar, A.P.: AS+EM+MS+TF-TuM1, 43; PS2-TuM5, 56
Pribil, G.K.: AS+EM+MS+TF-TuM10, 44
Prikhodko, S.: NS+BI-MoA3, 28
Principe, E.L.: AS1-ThM11, 165

Pringsheim, E.: BI+AS+BM+MS-WeM11, 121
Prinz, F.B.: EN-WeA7, **147**; TF3-MoA3, **39**
Priyadarshini, D.: SS2-TuM9, 61
Proksch, R.: EW-TuA5, 70
Protzman, J.: AS+EM+MS+TF-TuM12, 45
Puerta, J.M.: SS2-TuM1, 60
Pufall, M.R.: MS+GR+MI-ThM5, **175**
Pugmire, D.L.: SS1+AS+TF-ThM10, 182
Putkonen, M.I.: TF3-MoA10, **40**
Putnam, S.: SS1-WeA3, **156**
Putterman, S.: TR+SS-TuA3, **87**

— Q —

Qian, L.: EM-WeM10, **123**
Qiang, Y.: AS+NS-WeM5, 117
Qin, S.Y.: SS1-ThA2, 204
Qin, X.V.: PS-ThP12, **218**
Qiu, H.: SS1-MoM9, 16

— R —

Raadu, M.A.: SE2-MoM6, 14
Rack, P.D.: TF-ThM1, 184; TF-WeM4, 136
Rafati, A.: AS-ThA11, 187
Rahe, P.: SS-TuP18, 113
Rai, V.: TF2-TuA8, 85; VT-TuP17, 116
Raja, L.: PS2+TF-WeM12, 131
Raman, S.N.: AS-ThA10, 187; NS-ThA2, **198**
Ramana, C.V.: EM2-TuM1, 48; NS+BI-MoM6, 8; NS-TuP5, 101; TF1+PV-MoA1, 35; TF-WeA3, 159
Ramanathan, M.: MN+GR-ThM6, **174**
Ramanathan, S.: SS1-TuM5, 59
Ramaswamy, K.: PS1-TuM1, 53; PS1-WeM5, 128
Ramesh, R.: EM2-TuM4, **49**; EM2-TuM6, 49
Ramos, M.A.: NS-TuP5, 101
Ramos, R.: NS-ThM10, 176; NS-ThM2, **175**; PS2-ThA6, 202
Ramström, O.: NS-TuP6, 101
Randall, J.: SS1-MoM5, 16; SS1-MoM6, 16; VT-WeM3, 139
Rangan, S.: SS2-TuA11, 81; SS2-TuM5, 60
Ranson, P.: PS1-TuM12, 55; PS2-TuM11, 57
Rant, U.: BI+AS+BM+MS-WeM11, **121**
Raoux, S.: PS1-ThM11, 178
Rathbone, J.: EW-TuM8, 50; VT-MoA6, 41; VT-MoA8, 41; VT-TuP4, 114
Ratliff, J.S.: SS2-MoA8, 34
Ratner, D.: BI-ThP8, 210; SS2-FrM6, 245
Rauf, S.: PS1-TuM1, 53; PS1-TuM3, 53; PS1-WeA3, 153; PS1-WeA7, 153; PS1-WeA9, 154; PS1-WeM5, 128; PS2-ThM1, **179**; PS-ThP5, 217
Rauschenbach, B.: MI+TF-ThA9, 195; SE+TF-TuA7, 77; TF-ThP31, 229
Ravelosona, D.: MI+TF-ThA6, 194
Rawlett, A.: BI-MoA8, 26
Ray, M.P.: SS-ThP6, 220
Ray, V.: NS+BI-MoM11, 9; NS-WeM12, 127
Raynor, M.: NS-TuP1, 100
Rebecchi, C.: VT-MoM10, 23
Redondo-Morata, L.: AS2+BI-ThM11, **167**
Reed, A.: SE2-MoM10, 15
Reed, J.A.: BI-TuP4, **94**
Reedy, R.: MS-ThA8, 198
Rees, J.A.: PS-ThP9, **218**; SE2-MoM4, 14
Reeves, K.S.: AS-FrM9, 233; AS-WeM10, 120
Rego, R.: PS-TuP10, 107
Regonda, S.: NS-WeM4, 126
Rehammar, R.: AS-TuP17, 92
Reichertz, L.A.: EM-ThA9, 192
Reichling, M.: NS-ThM5, **176**; VT-TuP7, 114
Reimhult, E.O.: BI+AS+NS-ThA3, 187; BI+AS+NS-ThA8, 188; BI+AS+NS-WeA1, **144**
Reiner, J.: SS1+EM-MoA4, 32
Reinke, P.: GR-MoM8, **6**; SS1+EM-MoA11, 33; SS1-TuM5, 59
Ren, F.: EM-ThA10, 192
Ren, J.: SS1-TuM12, 59
Reniers, F.: PS2+TF-WeM1, 129; PS2+TF-WeM10, 131; PS-FrM2, **240**; PS-FrM8, 241; PS-TuP16, 108
Renzas, J.R.: NS-WeM6, 127; SS2-MoA11, 35
Repins, I.: EM-TuP6, 97
Reshchikov, M.A.: SS2-TuA3, 80
Restaino, D.: AS+EM+MS+TF-TuM12, 45
Reutt-Robey, J.: SS2-ThA2, 205
Rey, A.: NS2-TuA1, 73
Reyes-Vega, S.: AS-TuP29, 93
Reynolds, N.P.: SS2-ThA1, **205**
Rho, K.: PS1-WeM10, 129
Rhodes, C.: TF-ThM10, 185
Richardson, C.J.K.: GR+EM+MS-TuM6, 51
Richter, L.J.: AS+EM+MS+TF-MoM9, **3**
Ricks, M.: EW-WeL4, 141
Riehn, R.: BM+MN+MS+TF+BI-ThA8, **190**
Rietjens, G.H.: TF-FrM1, 246
Riisness, I.: NS-ThM10, 176; NS-ThM2, 175
Rincon, V.: EM-TuP16, 98; MN-ThP9, **216**
Rippard, W.H.: MS+GR+MI-ThM5, 175
Ritala, M.K.: TF2-MoM1, 20
Rittschof, D.: BI-TuA9, 68
Ritz, E.: PS1-WeM9, **129**
Rivers, J.: TF2-TuM6, **64**
Roberg, J.: PS1-WeM3, 128
Roberts, A.J.: TF1+PV-MoA3, **36**
Roberts, C.C.: SS2-MoA8, 34
Roberts, C.J.: BI-ThP20, 213; IJ+BI+MN+SE+AS-ThM10, 169
Roberts, N.K.: TF2-MoA6, 38
Robey, S.: SS2-ThA2, 205
Robinson, J.A.: GR+EM+MS-TuM4, 51; GR+SS-MoA10, 28; GR+SS-MoA3, 27; GR+SS-MoA7, **27**; GR+TF-TuA3, 71
Robinson, M.: AS-ThA2, 186
Rochford, J.: SS2-TuA11, 81
Roddy, M.A.: SE-TuP5, **110**
Rodil, S.E.: TF-ThP3, 223
Rodriguez, E.: SE-TuP6, 110
Rodriguez, J.A.: SS1-TuM9, 59; SS3-TuA1, **81**
Rodriguez, L.: TF-ThP3, 223
Rodríguez-Reyes, J.C.F.: SS-TuP3, **111**
Rogers, B.R.: AS-FrM11, **233**; TF-FrM5, 247
Rohde, S.L.: SE2-MoM11, 15
Roldan Cuenya, B.: NS-TuP14, 102; SS2-MoA10, 35; SS-TuP6, 112
Romero-Gomez, P.: TF1-TuA7, 83
Romero-Ortega, M.: BM+MN+MS+TF+BI-ThA3, 189
Roodenko, K.: MN-FrM9, 239
Roos, M.: SS2-ThA9, 206; SS2-ThM11, **184**
Roozeboom, F.: TF2-MoM5, 20
Röppischer, M.: AS+EM+MS+TF-TuM6, 44
Rosenberg, R.A.: NS-ThM1, **175**; SS-ThP5, 220
Rosenberg, S.: SS1+PS+TF+AS+NS-TuA1, 78
Rosenhahn, A.: BI-TuA8, **68**
Ross, P.N.: SS-TuP11, 113
Rossi, F.: AS2+BI-ThM6, 166; BI+AS+NS-FrM5, 234
Rossnagel, S.M.: TF-WeA1, **159**
Rotenberg, E.: GR+SS-MoA8, **28**; SS-TuP11, 113
Rothe, R.: PS2+PV-MoM4, 11
Roule, A.: AS+EM+MS+TF-TuM5, 43
Rousseau, M.: TF2-TuA10, 86
Routaboul, L.: BI+AS+NS-FrM6, 234
Rowlette, P.C.: PS2+TF-WeM2, 129; TF-ThA7, **208**; TF-WeA12, 161
Rowntree, P.A.: SS1+PS+TF+AS+NS-TuA9, **79**
Royer, J.E.: EM-TuP13, **98**
Rubal, M.: NS+BI-MoM1, 7
Rubloff, G.W.: EN-WeM9, **123**
Ruggeri, Z.M.: BI-MoA9, 26
Rumphorst, R.F.: PS1-ThM5, 177
Ruoff, R.S.: GR+TF-TuA10, 72; GR-MoM1, **5**
Rusavskii, A.: TF-ThP23, 227
Rushworth, S.: TF2-MoM5, 20
Russel, S.: SS2-WeM11, 134
Ruthenburg, T.C.: BI+AS+NS-WeA12, **145**
Rutherford, S.: HI-MoM5, **7**
Rutten, F.J.M.: SS1-WeA2, 156
Rutter, G.M.: NS-ThA8, 199
Ruzic, D.N.: PS1-WeM4, 128; PS1-WeM9, 129; SE2-MoM11, 15
Ryabova, E.: TF-ThP41, **230**
Ryan, E.T.: PS2+TF-WeM3, **130**
Ryan, P.J.: SS-ThP5, 220
Rybka, M.: AS-TuP19, 92
Ryu, S.: EM-TuP8, 97; TF-ThP4, 223

— S —

Saaem, I.: IJ+BI+MN+SE+AS-ThM11, **170**
Sachan, R.: TF-WeM9, 136
Sachrajda, A.: EM-ThA1, 191
Sadeghi, N.: PS2-ThA6, **202**; PS2-TuM11, 57; PS2-TuM9, 56
Sadowski, J.T.: SS1-FrM4, **242**
Saegusa, T.: NS+BI-MoA8, **29**
Saeki, T.: AS-TuP14, 91
Safarowsky, C.: SS2-ThM3, 182
Sahin, O.: BI+AS+BM+MS-WeM12, 121
Saini, G.: TF2-MoA1, **37**
Saint John, D.: AS+EM+MS+TF-MoM6, **2**
Saito, T.: NS+BI-MoA9, 29
Sakai, I.: PS2+MN-WeA7, **155**; PS-TuP7, 106
Sakai, M.: AS-TuP7, 90; SS-ThP12, 221; SS-ThP14, **222**; SS-ThP15, 222
Sakai, T.: SE1-MoM6, 13
Sakiyama, Y.: PS-FrM3, **240**
Sakurai, N.: PS2+MN-WeA7, 155
Sakurai, T.: SS1-FrM4, 242
Saldin, D.K.: SS2-MoM2, 17
Salis, G.: MI+EM-WeA12, 151
Salivati, N.: AS+NS-WeM3, **117**
Salmeron, M.: EM-WeM4, 122; IS+SS-ThM5, 171; SS1-WeA11, **157**; SS1-WeM10, 132; SS1-WeM12, 133; SS1-WeM4, 132; SS2-MoA11, 35; SS2-WeM5, 134; SS3-TuA8, 82; SS-ThP11, 221; SS-TuP8, 112
Salter, T.S.: AS1-ThM2, 164
Salvadori, M.C.: TF-WeM5, 136
Samha, H.: TF2-TuM5, 64
Samuelson, L.: SS1+EM-MoA7, 32
Samukawa, S.: PS1-ThM3, **177**; PS2+MN-WeA3, 155; PS2-ThA2, 202; PS2-ThM11, 180; PS-FrM10, 241; PS-TuA11, 76
Sanada, N.: AS-ThA9, 187
Sánchez-Mendieta, V.: AS-TuP29, 93
Sanchez-Valencia, J.R.: SE+TF-TuA10, 78
Sandstrom, A.M.: BI-TuP11, **95**
Sandt, P.: VT-MoA8, 41
Sanghavi, R.: NS-TuP32, 105
Sangiovanni, D.G.: TF1-TuA4, 83
Sankaran, R.M.: PS2-TuM1, **55**
Sankarapandian, M.: PS1-MoM8, 10
Sanno, Y.: TF-ThP11, **225**
Sansa, S.: TF-WeM12, 137
Sant, SP.: PS-TuA3, 75
Santos, B.: SS2-TuM1, 60
Sanz, F.: AS2+BI-ThM11, 167
Saraf, L.: IS+AS-ThA8, 193
Sarkar, A.: EM1+PV-TuM12, 48
Sarpatwari, K.: EM-WeA3, 146
Sarra-Bournet, C.: PS2-TuM3, 56
Sasaki, M.: PS1-TuM6, 54
Sathiyanarayanan, R.: SS1-ThA4, **204**
Sato, A.: PS1-TuM10, 54
Sato, H.: PS2+PV-MoM3, 11
Sato, M.: TF-ThP14, 225
Sato, Y.: EM-TuP7, 97; SE1-MoM8, 13; TF-FrM2, 246; TF-FrM7, 247; TF-FrM8, **247**; TF-ThP11, 225; TF-ThP12, 225; TF-ThP24, 227; TF-ThP27, 228; TF-ThP6, 224; TF-ThP9, 224
Sautter, K.: TF2-TuM5, 64; TF-WeM11, 136
Savu, V.: TF-ThA11, 208; TF-WeM12, **137**
Sawabe, M.: AS-TuP14, 91
Sawyer, G.: TR+SS-TuA7, 87
Sazhin, O.: VT-WeM10, **140**
Scammon, K.: AS1-ThM11, 165

Scarbrough, D.: IJ+BI+MN+SE+AS-ThM5, 169
Schaaf, P.: TF2-MoA4, 38
Schaff, O.: SS-TuP7, 112
Schamberger, F.: PS-FrM7, 240
Schaub, R.: GR+AS-WeA8, 148; NS+BI-MoA7, 29
Schiavone, P.: NS-ThA4, 199
Schiesko, L.: PS1-ThA1, 199
Schiess, A.: BM+MN+MS+TF+BI-ThA3, **189**
Schiffers, C.: TR+SE-WeA1, 161
Schilp, S.: BI-TuA8, 68; SS2-ThM5, **183**
Schirmeisen, A.: TR+NS-WeM1, 137
Schlaad, H.: SS2-FrM4, 244
Schlaf, R.: EM-TuP11, **97**; SS1-TuM1, 58
Schlittler, R.R.: MI+EM-WeA12, 151
Schlom, D.L.: EM2-TuM9, 49
Schmid, A.K.: IS+AS-FrM10, 236
Schmidt, B.W.: AS-FrM11, 233
Schmidt, D.: AS+EM+MS+TF-MoA3, **24**; SE+TF-TuA11, 78; TF1+SE-TuM6, 62
Schmidt, S.: SE2-MoM3, **14**; TR+SE-WeA1, 161
Schmitz, S.: MS-ThA6, 197
Schneider, J.M.: SE-TuM3, **58**; TF-ThM3, 184
Schoen, A.P.: NS2-TuA7, **74**
Schofield, N.: VT-MoM11, 23
Scholl, A.: BI-TuM6, 46
Schott, M.: EW-TuM8, 50; VT-MoA6, 41; VT-MoA8, **41**; VT-TuP4, 114
Schreiner, S.M.: BI-TuP15, 96
Schricker, S.: MN-ThP3, 215
Schriver, K.E.: TF-ThA6, 207
Schröder, H.: SS1+PS+TF+AS+NS-TuA12, 80
Schroeter, A.: TF-ThM4, **184**
Schrott, A.: PS1-ThM11, 178
Schubert, E.: AS+EM+MS+TF-MoA3, 24; AS-TuP20, 92; SE+TF-TuA11, 78; TF1+SE-TuM6, 62
Schubert, M.: AS+EM+MS+TF-MoA3, 24; AS+EM+MS+TF-MoM8, 3; AS-TuP20, 92; SE+TF-TuA11, **78**; TF1+SE-TuM6, 62
Schüpbach, B.: NS+BI-MoA10, 30
Schuller, I.K.: EM-TuP13, 98
Schultz, B.D.: PS2-TuM6, **56**
Schunk, D.: BI+AS+NS-ThA4, 188
Schvartzmann, M.: BI+AS+NS-FrM3, 234
Schwalb, C.H.: SS2-FrM8, 245
Schwarz, B.: PS-TuP1, 105
Schwarz, U.D.: NS-ThM9, **176**; TR+NS-WeM2, 137
Schwegler, E.: SS1-WeA12, 157; SS-ThP20, 223
Schwendemann, T.C.: NS-ThM9, 176; TR+NS-WeM2, 137
Schwöbel, J.: SS-ThP8, 221
Scoutaris, N.: IJ+BI+MN+SE+AS-ThM10, **169**
Seah, M.P.: AS1-ThM2, 164
Seal, S.: AS+NS-WeM10, 118; AS+NS-WeM11, 118
Seebauer, E.G.: MS-ThA3, **197**; SS2-FrM10, 246; SS-TuP13, 113
Seghete, D.: TF2-MoM3, **20**; TF2-TuA2, 84; TF2-TuA9, 85
Seifert, G.: TR+SS-TuA10, 87
Seitz, O.: NS-WeM4, 126; SS1-MoM5, 16
Seki, N.: PS2-ThM12, 181
Seki, T.: AS-ThA8, 187
Sekine, M.: PS-ThP11, 218; PS-TuP20, 109; PS-TuP7, 106
Seley, D.B.: MN+GR-ThM9, **174**
Self, W.T.: AS+NS-WeM10, 118
Sellmeyer, D.: SE+TF-TuA11, 78
Selwyn, G.S.: SE-MoA1, **30**
Semidey-Flecha, L.: TF1-TuA1, 83
Senanayake, S.: SS1-TuM9, 59
Sengupta, D.: BI-MoA6, **26**
Seo, H.: AS-TuP22, **92**
Seo, H.W.: TF1+SE-TuM4, 62
Seo, J.M.: SS-ThP1, 220; SS-ThP2, **220**
Seol, Y.G.: EM-WeM11, **123**
Seong, D.-J.: PS1-WeM10, 129
Seshabhattar, S.: TF-WeM4, **136**
Sessi, P.: GR-TuP4, 100
Sestak, M.N.: AS+EM+MS+TF-MoA6, 24; AS+EM+MS+TF-TuM11, **44**
Setina Batic, B.: NS-TuP12, **102**
Setsuhara, Y.: PS-ThP11, 218; PS-TuP20, 109
Settepani, P.: VT-WeA11, 163
Seymour, A.: NS-TuP1, 100
Seymour, D.L.: PS-ThP9, 218
Sezen, H.: AS-WeM1, 119
Sferrazza, M.: PS-FrM8, 241
Shah, K.: SS1-FrM8, 243
Shah, P.: EM-WeA2, **145**
Shah, R.K.: BI-TuP4, 94
Shamiryan, D.: PS2-ThA11, 203; PS-TuA7, 75
Shamloo, A.M.: BM+MN+MS+TF+BI-ThA9, **190**
Shan, T.R.: TR+SS-TuA8, **87**
Shannon, M.: MN+IJ+TR-ThA10, 197
Shaqfeh, E.S.G.: IJ+BI+MN-WeM11, **126**
Shard, A.G.: AS-ThA11, **187**
Sharipov, F.: VT-WeM5, 139
Sharp, J.C.: SS2-WeM6, **134**
Sharps, P.: EM1+PV-TuM9, **48**
Shavorskiy, A.: BI-TuM4, 45
Shearer, J.C.: TF-ThM5, **185**
Sheehan, P.: NS+BI-MoM5, **8**
Sheetz, M.P.: BI+AS+NS-FrM3, 234
Shekhah, O.: TF2-MoA3, **37**
Shelby, R.M.: PS1-ThM11, 178
Shen, C.: SS2-ThM6, **183**
Shen, C.Y.: SS1-ThA11, 205
Shen, J.: EM-TuP17, **98**; MI+TF-ThA11, 195; MI+TF-ThA4, 194; SS1+EM-MoA6, 32
Shen, J.L.: TF-ThP26, 228
Shen, M.: SS2-WeM11, 134
Shen, T.H.: MI+EM-WeA11, 151
Shenai, D.: TF2-TuA10, 86
Sheng, J.: EM1+PV-TuM11, 48; EM-TuP5, **97**
Shenk, T.: TR+NS-WeM11, **138**
Shenoy, V.B.: GR+AS-WeA3, 148
Shepperd, K.: SS1+PS+TF+AS+NS-TuA3, 79
Sherwood, P.: AS-WeM11, **120**
Shi, J.: MI+EM-WeA1, **150**
Shi, Y.: SS1-WeM10, 132; SS-ThP11, **221**
Shi, Z.: EM-WeM1, 121; EM-WeM9, 123
Shiao, M.H.: NS-TuP26, 104
Shields, J.: PS2-ThA10, **203**
Shigesato, Y.: EM-TuP7, **97**; SE1-MoM8, 13; TF-FrM2, 246; TF-FrM7, 247; TF-FrM8, 247; TF-ThP11, 225; TF-ThP12, 225; TF-ThP24, 227; TF-ThP27, 228; TF-ThP6, 224; TF-ThP9, 224
Shih, C.K.: SS1-ThA2, 204; SS2-TuM2, 60
Shim, H.: SS2-FrM3, **244**
Shim, W.B.: EM-TuP18, 98
Shimamura, K.: EM-ThM2, 167
Shimizu, T.K.: SS1-TuM4, **58**
Shimogaki, Y.: GR+EM+MS-TuM12, 52; TF2-TuM9, **64**
Shin, H.-J.: SS1-WeM3, **132**
Shin, J.H.: VT-TuP15, 115
Shin, K.: PS1-TuM1, 53
Shin, N.: AS+EM+MS+TF-MoM9, 3
Shin, S: TF-ThP29, 228
Shin, S.H.: AS-TuP2, 89
Shin, Y.-H.: PS1-WeM10, 129; VT-TuP15, 115
Shinde: TF-ThA3, **207**
Shindo, H.: PS1-WeM1, 127; PS2-ThM6, **180**
Shirai, Y.: EM2-TuM11, 50; VT-WeM4, 139
Shiratani, M.: PS2+PV-MoM3, 11; PS2+TF-WeM5, 130; PS-ThP11, 218; PS-TuP20, 109; PS-TuP21, **109**
Shirato, N.: TF-WeM9, 136
Shiro, M.: VT-WeM11, 140
Shivapooja, P.: BI-TuP3, **94**
Shkolnikov, M.: TF-ThP41, 230
Shoeb, J.: PS1-MoM6, **10**
Shohet, J.L.: EM-TuP19, **99**; PS1-ThA10, 201
Sholl, D.: TF1-TuA1, **83**
Shudy, D.F.: BI-TuP15, 96
Shukla, N.: NS+BI-MoM8, **8**
Shukur, H.: TF-ThP14, **225**
Shumaker-Parry, J.: BM+MN+MS+TF+BI-ThA6, **190**
Shutthanandan, V.: AS-FrM8, 233; AS-TuP23, 92; EM2-TuM1, 48; NS-TuP32, 105; SS1-FrM10, **244**; SS2-MoM11, 18; SS3-TuA11, 83; TF1+PV-MoA4, 36
Shyur, Y.: SS1+PS+TF+AS+NS-TuA11, **80**
Sidler, K.: TF-ThA11, 208
Silien, C.: NS+BI-MoA7, **29**; SS2-ThM6, 183
Simons, S.: BI-TuP7, 94
Simonyi, E.: PS2+TF-WeM3, 130
Simov, K.R.: SS1+EM-MoA11, 33
Simpson, M.L.: TF-WeM4, 136
Singer, I.L.: TR+SS-TuA2, 86
Singh, H.: PS+MS-MoA6, 30; PS1-TuM10, 54
Singh, K.A.: EM-WeM6, **122**
Singh, P.: SS1-FrM10, 244
Singh, S.: AS+NS-WeM10, 118
Singler, T.: IJ+MN+TF-WeA10, 149
Sinnott, S.B.: NS+TR-TuM2, 52; TR+SS-TuA7, 87; TR+SS-TuA8, 87; TR+SS-TuA9, **87**
Sirard, S.: PS2-ThM11, 180
Sirghi, L.: AS2+BI-ThM6, 166
Sisk, D.R.: AS-WeM12, 120
Sit, J.C.: TF1+SE-TuM9, 62
Sitnitsky, I.L.: AS-WeM9, 120
Sivaraman, B.: BI-MoA10, **26**
Sjövall, P.: BI+AS+NS-WeA4, 144
Skomski, R.: SE+TF-TuA11, 78
Skuza, J.R.: MI-ThM1, **172**
Slaughter, M.M.: MN-ThP5, 215
Smekal, W.: AS-WeA3, 142
Smentkowski, V.S.: AS-TuP24, **93**
Smets, A.H.M.: PS2+PV-MoM5, **11**
Smith, A.: MI+EM-WeA8, 151
Smith, D.A.: VT-MoM1, **21**
Smith, D.R.: BI+AS+NS-WeA10, 145
Smith, N.: GR+MI-WeM2, 124
Smith, R.A.P.: AS-FrM5, 232
Smith, R.S.: SS1-WeA9, 156; SS-ThP7, 221
Smith, W.: TF1+SE-TuM3, **61**
Sniegowski, J.J.: AS-FrM10, 233
Snyder, D.: GR+SS-MoA7, 27
Snyders, R.: TF2-MoA2, 37
Sobahan, K.M.A.: SE-TuP1, 109; SE-TuP2, **110**
Sobbia, R.: PS2+PV-MoM9, 12
Sobek, J.: BI+AS+NS-ThA3, 187
Sobol, P.: AS1-ThM11, 165
Sobolewski, M.A.: PS-TuP9, **107**
Sogo, S.: VT-MoM5, 22
Sokolov, D.: SS1+PS+TF+AS+NS-TuA3, 79
Solanki, R.: GR+TF-TuA11, 72
Sologubenko, A.: SS2-ThM12, 184
Somorjai, G.A.: AS-TuP22, 92; IS+SS-ThM2, 170; NS-WeM6, 127; SS2-MoA11, 35
Son, J.Y.: AS-WeA11, 143
Son, Y.K.: TF-ThP39, 230
Son, Y.-W.: GR+MI-WeM9, **125**
Song, J.: NS+BI-MoA4, **29**
Song, J.D.: AS-TuP2, 89; AS-TuP3, 89
Song, Y.J.: NS-ThA8, **199**; NS-TuP15, 102
Sonnet, A.M.: SS1+EM-MoA1, 31
Sorensen, D.N.: SS1+AS+TF-ThM9, 182
Sorge, J.B.: TF-ThP17, **226**
Sosolik, C.E.: SS-ThP6, 220
Soulan, S.: NS-ThA4, 199
Spangenburg, M.: MI+EM-WeA11, 151
Spencer, N.D.: NS2-TuA1, 73
Sperling, B.A.: AS+EM+MS+TF-MoA8, 24; TF-ThP34, **229**
Spool, A.M.: AS1-ThM10, **165**
Sproul, W.D.: SE2-MoM4, **14**
Sprunger, P.: SS2-MoM10, 18
Squires, K.H.: SS1-MoM1, 15
Sriraman, S.: PS1-TuM10, 54
Srivastava, N.: GR+SS-MoA6, 27
Stacchiola, D.J.: SS1-TuM9, 59; SS3-TuA1, 81

Stacey, K.: MN+IJ+TR-ThA10, 197
Stafford, L.: PS2-ThA3, 202; PS2-ThM10, 180; PS-FrM9, 241; PS-TuA1, 74
Staggs, K.: BI-TuP2, **94**
Stamenkovic, V.: SS-TuP11, 113
Standaert, T.: MS-ThA6, 197
Stanley, S.: TF-FrM9, 247
St-Antoine, B.C.: GR+EM+MS-TuM3, 51
Stanton, C.: MI+EM-WeA4, 150
Starostin, S.A.: AS+EM+MS+TF-TuM1, 43; PS2-TuM5, **56**
Starr, D.: SS1-WeM4, 132
Stass, I.: SS1-WeA11, 157; SS1-WeM12, 133; SS2-WeM5, **134**
Stayton, P.S.: AS-ThA2, 186
Steeves, M.M.: TF1-MoM5, **19**
Stefanakos, E.: TF-ThP21, 227
Steinrueck, H.-P.: SS2-WeM6, 134
Stellacci, F.: BI+NS-MoM3, **4**
Stepanov, V.: TF-ThP23, 227
Stephens, J.: SS2-TuM12, **61**
Sternberg, M.: NS1+PV-TuA7, 73
Stevens, B.L.: TF1+SE-TuM11, **63**
Stevenson, K.J.: AS+EM+MS+TF-MoA4, 24
Stillahn, J.M.: PS2+TF-WeM9, **130**
Stocker, R.: VT-MoA1, 40
Stöhr, M.: SS2-ThA1, 205; SS2-ThA7, **206**
Stoke, J.A.: AS+EM+MS+TF-MoA6, 24
Stokes, D.: IS+AS-FrM7, 235
Stoltz, P.H.: EW-WeL5, 141
Stosch, R.: SS2-ThM12, 184
Stout, P.J.: PS1-TuM1, 53; PS1-TuM3, 53; PS1-WeA3, **153**; PS1-WeA7, 153
Strader, J.: TF-WeM9, 136
Strasser, P.: SS3-TuA7, 82
Streifer, J.: SS2-FrM5, 245
Streng, D.E.: BM+MN+MS+TF+BI-ThA8, 190
Strohmeier, B.R.: AS+NS-TuA4, 67; AS+NS-WeM2, **117**; AS-TuP10, 90; EW-WeM8, **124**
Strongin, D.R.: SS1-WeA7, **156**
Stroscio, J.A.: GR+MI-WeM12, 125; GR+MI-WeM5, 124; GR+SS-MoA1, **27**; NS-ThA8, 199; NS-TuP15, 102
Strunz, T.: AS2+BI-ThM4, 166
Struyf, H.: PS-TuA7, 75
Stuart, S.J.: BI-TuP12, 95
Studenikin, S.: EM-ThA1, 191
Su, C.Y.: EM-TuP3, 96; NS-TuP26, **104**; TF-ThP30, 229
Subramanian, R.: NS+BI-MoM11, **9**; NS-WeM12, 127
Sugai, H.: PS-ThP10, 218
Sugawa, S.: EM2-TuM11, 50
Sugimura, H.: AS-TuP16, 91; AS-TuP4, 89; AS-TuP6, 90; NS-TuP13, 102
Sukegawa, T.: AS-TuP8, 90
Sullivan, S.: BI-MoA7, 26
Sumant, A.V.: MN+GR-ThM10, **174**; MN+GR-ThM6, 174; MN+GR-ThM9, 174; MN-FrM10, 239
Sun, B.: VT-TuP5, **114**
Sun, D.: SS2-WeA7, 158
Sun, J.: AS+EM+MS+TF-TuM10, 44
Sun, Y.: EM-TuA7, **69**; GR+SS-MoA6, 27; IJ+BI+MN+SE+AS-ThM12, **170**; IJ+MN+TF-WeA10, 149
Sundaramoorthy, R.: EM-TuP6, 97
Sundararajan, R.: PS2-ThA4, 202; PS-ThP17, 219
Sung, C.Y.: MS+GR+MI-ThM11, **175**
Sung, J.C.: GR+AS-WeA11, **149**
Sung, M.: GR+AS-WeA11, 149
Sur, J.C.: EM-TuP23, 99
Surman, D.J.: AS-WeA7, 142; EW-TuL5, **66**
Sushko, M.: AS2+BI-ThM4, 166
Sutter, E.A.: GR-MoM6, 6
Sutter, P.W.: GR-MoM6, 6; SS2-MoM5, 18
Suydam, J.: TF2-TuA10, 86
Suzer, S.: AS-WeM1, **119**
Suzuki, A.: AS-TuP24, 93
Suzuki, H.: EM2-TuM11, 50; MN-ThP2, 215
Suzuki, M.: AS-ThA9, 187; AS-WeA11, 143; SE+TF-TuA4, **77**
Suzuki, T.: GR-MoM11, 6
Svedhem, S.: BI+AS+NS-WeA4, 144
Swanson, K.R.: AS-WeM12, 120
Swart, H.C.: TF1-MoM2, 19
Swartzentruber, B.S.: SS1-ThA10, **205**
Syed, S.: BI+AS+NS-ThA6, 188
Sykes, C.E.: SS2-WeA3, **158**
Syssoev, S.E.: VT-MoM8, **22**
Szakal, C.: AS1-ThM6, 164
Szanyi, J.: SS1-MoM10, 17; SS1-TuM6, 59; SS3-TuA11, 83
Szelagowska-Kunstman, K.: NS+BI-MoA10, **30**; NS-TuP29, 104
Szlufarska, I.: TR+NS-WeM3, **137**
Szymonski, M.: NS-TuP29, 104

— T —

Tabuchi, R.: SE+TF-TuA4, 77
Tadidagapa, S.: BI+AS+NS-WeA9, 145
Tadisina, Z.R.: MI+TF-ThA8, **195**
Taggart, D.K.: EM1+PV-TuM3, 47
Taguchi, Y.: AS-TuP6, 90
Taha, H.: EW-TuA6, 70; NS-ThA1, 198
Tai, L.: AS+EM+MS+TF-TuM12, 45
Taing, J.: SS-ThP16, 222
Tait, S.L.: SS2-ThA10, 207; SS2-ThA11, **207**
Takahashi, H: AS-WeA11, 143
Takahashi, H.: BI+AS+NS-ThA9, 189; BI-ThP13, 211
Takahashi, M.: MN-ThP1, 215
Takahashi, T.: TF-ThM3, **184**
Takami, T.: SS-ThP9, 221
Takano, I.: TF-ThP14, 225; TF-ThP2, 223; TF-ThP7, 224; TF-ThP8, 224
Takasaki, A.: TF-ThP24, **227**
Takeda, K.: PS-ThP11, 218; PS-TuP7, 106
Takeda, S.: TF-ThP10, 225
Takeguchi, M.: PS-FrM10, 241
Takeshita, K.: PS2-ThM11, 180
Taketoshi, N.: TF-ThP27, 228
Takeuchi, E.: NS-TuP20, 103
Takeuchi, M.: SE1-MoM1, **12**
Talledo Coronado, A.F.: TF-WeM6, **136**
Tan, C.: MN-FrM3, 238
Tanaka, H.: EM-WeM3, 122
Tanaka, K.: TF-ThP8, **224**
Tang, J.: MI+EM-WeA7, **150**
Tang, L.: SS1-FrM1, 242
Tang, W.: TR+SS-TuA11, **87**
Tang, X.: MS-ThA4, 197
Tang, Z.Z.: TF1+PV-MoA10, 37
Taniguchi, Y.: AS-TuP6, 90
Tao, F.: SS2-MoA11, **35**; TF-WeM1, **135**
Tartis, M.: BI-TuP2, 94
Tasaki, C.: TF-ThP11, 225
Taschuk, M.T.: SE+TF-TuA9, **77**
Tashiro, Y.: SS-TuP10, 112
Tatarchuk, I.: TF-ThP23, 227
Tatsumi, T.: PS1-TuM9, 54; PS2+MN-WeA3, 155
Taylor, M.: BI-MoA3, 25
Techane, S.D.: AS+NS-WeM9, **118**
Tedesco, J.L.: GR+EM+MS-TuM4, 51; GR+SS-MoA3, 27; GR+TF-TuA3, **71**
Teixeira, F.S.: TF-WeM5, **136**
Tendler, S.J.B.: BI-ThP20, 213
Tenne, R.: TR+SS-TuA10, 87
Tenney, S.A.: SS2-MoA8, 34
Tennyson, J.: PS-ThP2, 217
Teplyakov, A.V.: SS1-MoM3, **16**; SS-TuP3, 111; SS-TuP4, 111
ter Veen, H.R.J.: AS-FrM5, 232
Teramoto, A.: EM2-TuM11, 50
Teraoka, Y.: AS-TuP9, 90
Terfort, A.: BI+AS+NS-ThA10, 189; NS+BI-MoA10, 30
Terlinden, N.M.: AS+EM+MS+TF-MoM2, 2; SS2-FrM2, **244**
Terminello, L.J.: MI+TF-ThA10, 195
Terrell, E.A.: MN+GR-ThM9, 174
Terryn, H.: PS2+TF-WeM1, 129; TF2-MoA2, 37
Teslich Jr., N.E.: TF2-TuM12, 65
Textor, M.: BI+AS+NS-ThA3, 187; BI+AS+NS-ThA8, 188
Thapa, T.: BI-TuP7, **94**
Theilacker, W.: BI-MoA7, 26
Theodore, N.: TR+SE-WeA9, **161**
Therien, M.J.: NS1+PV-TuA4, 73; NS-WeM10, 127; NS-WeM3, 126
Thevuthasan, S.: AS+NS-WeM11, 118; EM-WeM6, 122; IS+AS-ThA8, 193; IS+SS-ThM6, 171; NS-TuP32, 105; SS1-FrM10, 244; SS2-MoM11, 18; SS3-TuA11, 83
Thiel, P.A.: SS1-ThA3, 204; SS2-WeM11, 134
Thiry, D.: TF2-MoA2, 37
Thissen, A.: EW-WeL6, **141**; SS-TuP7, **112**
Thomas, H.: BI+AS+NS-ThA10, 189
Thompson, J.D.W.: MI+EM-WeA11, 151
Thompson, P.E.: MI+EM-WeA9, 151
Thornberg, S.: VT-MoA2, **40**
Thornberry, C.: AS+EM+MS+TF-TuM11, 44
Thorpe, R.: SS2-TuA11, 81
Thorsteinsson, E.G.: PS1-WeA8, 154
Thrower, J.D.: SS1-WeA2, 156
Thürmer, K.: GR+AS-WeA9, 148; SS1-WeM11, **133**
Tian, C.Z.: PS2-ThM9, 180; PS-ThP17, 219
Tian, J.: IJ+BI+MN+SE+AS-ThM11, 170
Tian, R.: NS-WeM4, 126
Tian, W.C.: MN+IJ+TR-ThA10, **197**
Timm, R.: SS1+EM-MoA7, 32
Ting, Y.-H.: PS-ThP12, 218
Tischler, J.G.: EM-ThA2, 191; GR+SS-MoA3, 27
Tischler, J.Z.: MI+TF-ThA4, 194
Tisone, T.C.: BI+AS+BM+MS-WeM5, **121**
Titus, M.J.: PS-TuA8, **75**
Tiwald, T.E.: AS+EM+MS+TF-MoA9, 25; AS+EM+MS+TF-TuM10, 44
Tizazu, G.: BI-ThP9, 210
Tjong, V.: BI-ThP12, **211**
Tobias, D.: SS1-WeM9, 132
Tobin, J.G.: MI+EM-WeA11, **151**; MI-ThM6, 173
Tode, M.: AS-TuP9, 90
Todorova, M.: SS2-TuA10, 81
Todorow, V.: PS1-TuM1, 53
Tokashiki, K.: PS1-TuM1, 53
Tokumasu, F.: AS2+BI-ThM10, 167
Tomanek, D.: SS2-ThA6, 206
Tombros, N.: GR+MI-WeM3, **124**
Tomita, T.: VT-TuP16, 116
Tomsic, A.: SS1+PS+TF+AS+NS-TuA12, 80
Toney, M.: SS3-TuA7, 82
Topple, J.: TF1-TuA11, **84**
Torres, R.: NS-TuP1, 100
Torres, R.D.: TF-ThA2, **207**
Torres, T.: SS1-FrM2, 242
Tosa, M.: MN-ThP2, 215
Tougaard, S.: AS-WeM12, 120
Touzeau, M.: PS2-ThA6, 202
Toyoda, S.: AS-TuP8, **90**
Tran, N.: SS2-WeM2, 133
Tran, N.H.: TF2-MoA6, 38
Tran, T.: SS1-WeM1, 131
Tratnyek, P.G.: AS+NS-WeM5, 117
Trelka, M.: MI-FrM5, 237; SS1-FrM2, **242**; SS2-ThA10, 207; SS2-ThM10, 183
Trenary, M.: SS2-MoA9, 34; SS2-TuM6, 60; SS2-WeM4, **134**
Trevino, K.: PS1-ThM12, **178**
Trillwood, E.: VT-TuP18, **116**
Triplett, B.B.: EM-TuP19, 99
Tripp, C.P.: SS1+AS+TF-ThM5, **181**
Trivedi, K.: NS1+PV-TuA3, 72; NS-WeM4, 126
Tröger, L.: VT-TuP7, **114**
Trogler, W.C.: EM-TuP13, 98
Troitskaia, I.B.: NS-TuP5, **101**
Trouillet, V.: AS-TuP1, 89

Trufan, E.: SS2-MoA9, 34
Trumbull, K.: GR+SS-MoA10, 28; GR+SS-MoA7, 27
Tsai, C.H.: NS-TuP23, 104
Tsai, D.P.: EM-TuP1, 96; EM-TuP3, 96; TF-ThP22, 227
Tsai, M.Y.: TF-ThP30, 229
Tsai, W.: EM-TuA7, 69
Tseng, C.C.: SS-TuP19, **113**
Tseng, T.-C.: SS2-ThA10, 207
Tskipuri, L.: SS2-TuM5, 60
Tsuda, H.: PS1-ThA8, **201**; PS1-ThM9, 178
Tsuji, H.: TF-FrM2, 246
Tsukada, M.: SS1-WeM2, **131**
Tsukamoto, N.: TF-FrM7, 247; TF-ThP12, 225; TF-ThP6, **224**; TF-ThP9, 224
Tsung, C.: SS2-MoA11, 35
Tudosa, I.: MI+TF-ThA6, 194
Tung, F.C.: PS-ThP7, **217**
Turchanin, A.: SS2-ThM12, **184**
Turner, K.: MN-FrM1, **238**
Turner, M.M.: PS2-ThA9, 203; PS-ThP15, **219**
Tutt, L.W.: TF3-MoA8, 40
Twiss, J.: BI-MoA7, 26
Tyagi, A.: BM-ThP3, **213**
Tyagi, P.V.: AS-TuP14, **91**

— U —

Uder, B.: NS-ThA6, 199
Ueda, Y.: PS1-ThM9, 178
Uenishi, S.: NS-TuP13, **102**
Ueno, S.: TR+SS-TuA1, 86
Uhl, A.: SS2-MoA9, **34**
Ulfig, R.M.: TF2-MoM4, 20
Ulloa, S.E.: MI-FrM6, **237**
Umetsu, J.: PS-TuP20, 109
Unal, B.: SS1-ThA3, 204
Uraoka, Y.: PS-FrM10, 241
Urban, C.: MI-FrM5, 237; SS1-FrM2, 242; SS2-ThA10, 207; SS2-ThM10, **183**
Urban, F.K.: AS+EM+MS+TF-MoA9, **25**
Urbanowicz, A.: PS-TuA7, 75
Uritsky, Y.: AS-WeA9, 143; MS-ThA4, 197
Urquhart, A.J.: BI-MoA3, 25
Utada, A.S.: IJ+BI+MN-WeM5, 125
Utsuno, F.: TF-ThP24, 227
Utz, A.L.: SS2-WeA10, **158**
Uvdal, P.E.: SS1-WeA4, **156**

— V —

V Nampoori, H.: EM-TuP16, 98; VT-TuP12, **115**
Vaeth, K.: IJ+MN+TF-WeA7, 149
Vahedi, V.: PS+MS-MoA6, **30**; PS1-TuM10, 54
Vail, M.A.: TF2-MoA1, 37
Vallee, C.: TF2-MoA9, **38**
Vallée, C.: AS+EM+MS+TF-TuM5, 43
Valles-Rosales, D.: AS-FrM4, 232
Vallier, L.: PS1-ThA7, 200
Valougeorgis, D.: VT-WeM5, 139
Valsesia, A.: AS2+BI-ThM6, 166; BI+AS+NS-FrM5, 234
Valtiner, M.: SS2-TuA10, **81**
Van Antwerp, K.: EW-TuM8, **50**; VT-MoA6, 41; VT-MoA8, 41; VT-TuP4, 114
van Assche, F.J.H.: TF-FrM1, **246**
van Buuren, T.: AS+NS-TuA1, 67; MI+TF-ThA10, 195
Van De Keere, I.: TF2-MoA2, 37
van de Sanden, M.C.M.: AS+EM+MS+TF-MoA10, 25; AS+EM+MS+TF-MoM2, 2; AS+EM+MS+TF-TuM1, 43; AS+EM+MS+TF-TuM9, 44; EM1+PV-TuM12, 48; PS1-ThA3, 200; PS1-ThM5, 177; PS2+PV-MoM5, 11; PS2+PV-MoM8, **12**; PS2-TuM5, 56; PS-TuP10, 107; SS1+PS+TF+AS+NS-TuA8, 79; SS2-FrM2, 244; TF2-MoM5, 20; TF2-TuM11, 64; TF3-MoA7, 39; TF-ThA8, 208
van de Weijer, P.: TF2-TuM11, 64; TF-FrM1, 246
van Dorp, W.F.: SS1+PS+TF+AS+NS-TuA1, 78; SS1+PS+TF+AS+NS-TuA7, **79**
van Mol, A.M.B.: TF-FrM1, 246
van Schilfgaarde, M.: TF1+PV-MoA10, 37
van 't Erve, O.M.J.: MI+EM-WeA9, **151**; MI-ThP5, 214
van Wees, B.J.: GR+MI-WeM3, 124
van Zeijl, E.: VT-MoM4, 22
Vanderford, J.: VT-TuP11, **115**
Vane, R.: VT-MoM3, 22
Vanfleet, R.: MN+GR-ThM5, 174; NS+BI-MoA4, 29
Vangeneugden, D.: PS-TuP10, 107
Vaniapura, V.: PS1-TuM11, 55
VanWerven, E.C.: MN-ThP7, 216
Vanzetti, L.E.: BM-ThP4, 213
Varoutis, S.: VT-WeA3, **162**; VT-WeM5, **139**
Vasin, A.: TF-ThP23, 227
Vásquez Mazzoti, D.G.: TF-WeM6, 136
Vazquez de Parga, A.L.: GR+AS-WeA7, **148**; GR+TF-TuA4, 71
Vazquez-Mena, O.: TF-ThA11, 208
Veal, T.D.: EM-ThM3, **167**
Végh, J.J.: PS1-ThA9, 201; PS-TuA12, 76; PS-TuA9, 75
Veitzer, S.: EW-WeL5, 141
Vempaire, D.: PS2-ThA6, 202
Vemuri, R.S.: EM2-TuM1, 48; TF1+PV-MoA1, **35**
Venkatasubramanian, C.: TF1-MoM9, **19**
Ventrice, C.A.: GR+TF-TuA10, **72**
Verbeck, G.F.: SS1-FrM6, **243**
Verboncoeur, J.: TF1-TuA10, 84
Verbridge, S.S.: MN-FrM8, 239
Vereecken, J.: PS2+TF-WeM1, 129
Verkuijlen, R.O.F.: TF2-MoM5, 20
Verlaan, V.: SS2-FrM2, 244; TF-ThA8, 208
Verma, P.: BI-ThP19, **212**
Verove, C.: PS1-MoM10, 10; PS1-MoM11, 10; PS1-MoM5, 9; PS1-TuM5, 54
Versluis, R.: VT-WeM6, **139**
Veyan, J.-F.: MN-FrM9, **239**; SS1-MoM5, 16; SS1-MoM6, 16
Vick, D.: TF1+SE-TuM12, 63
Vijayalakshmi, S.: NS-ThM1, 175
Villanueva, L.G.: TF-ThA11, **208**
Villermaux, E.: IJ+BI+MN-WeM3, **125**
Villora, E.G.: EM-ThM2, 167
Vinckier, C.: PS2-ThA11, 203
Viswanath, R.N.: NS-WeM5, 126
Vo-Dinh, T.: NS-WeM9, 127
Voeroes, J.: BI+AS+NS-ThA6, 188
Voevodin, A.: SE2-MoM10, 15
Vogel, E.M.: NS-WeM4, 126; SS1+EM-MoA1, 31
Vogtli, M.: AS2+BI-ThM4, 166
Voros, J.: TF2-MoA4, 38

— W —

Waddill, G.D.: MI+EM-WeA11, 151; MI-ThM6, **173**
Waggoner, P.: MN-FrM3, **238**
Wagner, H.D.: BI-ThP6, 210; TR+SS-TuA10, 87
Wagner, J.B.: SS1+PS+TF+AS+NS-TuA7, 79
Wahl, K.J.: BI-TuA9, 68; TR+SE-WeA9, 161; TR+SS-TuA2, **86**
Wahl, M.: SS2-ThA7, 206
Waite, A.: SE2-MoM10, 15
Wakefield, N.G.: TF1+SE-TuM9, **62**
Waldmann, T.: SS2-ThA9, **206**; SS2-ThM11, 184
Walker, A.V.: EM-WeM9, **123**
Walker, F.J.: SS1+EM-MoA4, 32
Wallace, D.B.: IJ+BI+MN+SE+AS-ThM1, **169**
Wallace, R.M.: EM-TuA10, 70; EM-TuA8, 69; GR+AS-WeA10, 148; SS1+EM-MoA1, 31; SS1-MoM5, 16; SS1-MoM6, 16; TF2-TuA10, 86; VT-WeM3, 139
Walls, J.M.: TF-FrM9, **247**
Walters, D.R.: PS2+TF-WeM11, **131**
Waltman, R.: AS1-ThM10, 165
Walton, C.: TF1-TuA10, **84**
Walton, S.G.: AS-FrM7, 233; AS-WeA8, 143; GR-MoM5, **5**; GR-TuP1, 100; PS-TuA2, 75
Walukiewicz, W.: EM-ThA9, 192
Waly, N.: BI-ThP11, 211
Wan, A.: EM-TuA3, **69**; EM-TuA4, 69; EM-TuA9, 70
Wan, H.L.: SS1-MoM11, 17
Wandelt, K.: SS1-TuM10, 59; SS2-ThM2, 182; SS2-ThM3, **182**; SS2-TuM10, 61
Wang, B.: GR+AS-WeA8, 148; NS+BI-MoA7, 29
Wang, C.C.: MS-ThA4, **197**
Wang, C.M.: AS+NS-WeM5, 117; IS+AS-ThA8, **193**
Wang, D.: PS-TuA10, 76; PS-TuA9, 75
Wang, F.: SS2-MoM10, 18
Wang, G.: NS-WeA4, 152
Wang, H.: BI-ThP1, **210**; TF2-MoA3, 37; TF2-MoM4, 20
Wang, J.: SE2-MoM4, 14; SS1+PS+TF+AS+NS-TuA11, 80
Wang, L.: AS-FrM6, 232
Wang, M.: PS1-ThM2, **177**
Wang, P.: SS1-FrM5, 242
Wang, Q.H.: GR+EM+MS-TuM11, **52**; SS-TuP5, **112**
Wang, S.: MI+TF-ThA8, 195
Wang, T.: TF2-TuA12, **86**
Wang, W.: EM-TuP9, 97; MI+EM-WeA7, 150; TF-WeA11, 160
Wang, X.: BI-ThP1, 210; MI+EM-WeA7, 150; NS-TuP6, **101**; SS1-MoM11, 17; SS2-FrM5, **245**; TF2-MoM4, 20
Wang, X.P.: MN+GR-ThM10, 174
Wang, Y.: BM-ThP2, **213**; MI-FrM3, 236; MS-ThA1, 197; SS1-MoM9, **16**
Wang, Y.M.: TF2-TuM12, 65
Wang, Z.L.: NS-ThM1, 175
Ward, D.J.: SS2-WeA1, **157**
Ward, T.Z.: MI+TF-ThA4, **194**
Wark, D.: AS-TuP24, 93
Warman, M.: BI-TuP10, 95
Washington, J.S.: PS1-ThM11, **178**
Watahiki, K.: GR-MoM11, 6
Watanabe, D.: TF-ThP6, 224
Watanabe, H.: TF-FrM2, 246
Watanabe, T.: AS-TuP7, 90; SE-TuM6, **58**; SS-ThP15, 222
Watanuki, K.: EM2-TuM11, **50**
Watson, D.G.: NS-ThA2, 198
Waugh, A.R.: TF-FrM9, 247
Weaver, J.F.: SS1-TuM11, **59**
Weber, J.W.: AS+EM+MS+TF-TuM9, **44**; PS1-ThA3, 200
Weckhuysen, B.M.: IS+AS-ThA3, 193
Wedlich, D.: AS-TuP1, 89
Wegner, D.: MI-FrM3, 236
Wehbe, N.: AS-TuP13, 91
Wei, D.: PS2-ThM11, 180
Wei, T.C.: PS-ThP7, 217
Wei, Y.: SS2-ThA2, **205**
Weidner, T.: AS+NS-WeM4, 117; BI-TuM9, **46**; SS2-FrM6, 245
Weiland, B.E.: GR+SS-MoA10, 28
Weilnboeck, F.: PS-TuA10, 76; PS-TuA12, 76; PS-TuA9, 75
Weimann, T.: SS2-ThM12, 184
Weiss, P.S.: AS+NS-TuA9, 68; BI+NS-MoM2, 4; EM-TuP26, 99
Weiss, S.: TF-FrM5, 247
Weissmüller, J.: NS-WeM5, 126
Weitz, D.A.: BI-TuP4, 94; IJ+BI+MN-WeM5, 125
Wellinghoff, S.: NS+BI-MoM1, 7
Wen, J.: SS1-TuM3, 58
Wen, X.: BI-ThP14, 211
Wendt, A.E.: PS-ThP12, 218
Wendt, S.: SS3-TuA8, 82
Wenkin, M.: PS2+TF-WeM1, 129
Werner, C.: AS+EM+MS+TF-TuM6, 44
Werner, W.S.M.: AS-WeA3, 142

Wessels, J.: NS+BI-MoA6, 29
Wetherington, M.: GR+SS-MoA7, 27
White, M.: SS2-WeM3, 133; SS3-TuA4, 82
White, R.: AS1-ThM10, 165
White, R.G.: AS+NS-WeM2, 117; AS-FrM7, 233; AS-FrM9, 233; AS-TuP1, 89; AS-WeA8, **143**; AS-WeM10, 120; EW-TuL3, **66**
Wickard, T.: SS2-FrM4, 244
Widjaja, N.: MI+TF-ThA11, 195
Wiecinski, P.: AS+NS-WeM12, 119
Wieckowski, A.: SS2-WeM12, 135
Wieringa, F.P.: PS-FrM5, 240
Wiesendanger, R.: MI-FrM4, 237; SS2-ThA8, 206; SS-ThP10, 221; SS-ThP8, 221
Wiest, L.A.: TF2-MoA1, 37
Wiggins, B.C.: NS+BI-MoM10, 8
Wikfeldt, K.T.: IS+AS-ThA2, 193
Wild, C.: TF2-TuM12, 65
Wilks, S.: TF1-TuA10, 84
Willey, T.M.: AS+NS-TuA1, **67**
Williams, E.: GR+SS-MoA4, 27
Williams, N.: PS1-TuM10, 54
Williamson, T.L.: EM-ThA9, **192**
Willingham, D.G.: AS1-ThM9, 165
Willis, D.: BI-MoA7, 26
Willson, C.G.: PS-TuA12, 76
Wilson, K.: VT-WeA11, 163
Wilson, W.: MS-ThA8, 198
Wimplinger, M.: AS+EM+MS+TF-TuM2, 43; SE-TuP7, 110
Wincheski, B.: MI-ThM1, 172
Wind, S.J.: BI+AS+NS-FrM3, 234
Windisch Jr., C.H.: AS+NS-WeM11, 118
Wingren, C.: BI+AS+BM+MS-WeM1, **120**
Winkler, K.: AS-WeM2, 119; NS-ThA6, **199**
Winkler, T.: BI+AS+NS-ThA10, 189
Winograd, N.: AS1-ThM9, 165
Winter, B.: SS1-WeM9, 132
Winter, R.: TR+NS-WeM11, 138
Wintjes, N.: SS2-ThA1, 205
Wisbey, D.S.: NS-ThA3, 198
Wise, R.: PS+MS-MoA1, **30**
Wittstock, A.: NS-WeM5, 126
Wnuk, J.: SS1+PS+TF+AS+NS-TuA1, 78
Wode, F.: BI-TuA8, 68
Wodtke, A.M.: SS2-WeA11, 158
Woell, Ch.: SS-TuP18, 113; TF2-MoA3, 37
Wolak, M.: EM-TuP11, 97; SS1-TuM1, 58
Wolden, C.A.: PS1-WeM2, 128; PS2+TF-WeM2, **129**; TF2-TuA4, 85; TF-ThA7, 208; TF-WeA12, 161
Wolf, H.: NS2-TuA1, **73**
Wolf, S.: SS1-TuM5, 59
Wolkow, R.: NS-WeM11, 127
Woll, A.R.: SS1-FrM3, 242
Wöll, Ch.: SS1-MoM9, 16; SS2-WeM12, 135
Wolstenholme, J.: AS-WeA8, 143; EW-TuL3, 66
Wolter, S.D.: SS2-TuA1, 80
Womack, F.: SS2-MoM10, 18
Wong, K.T.: SS1-MoM2, 15
Wong, M.S.: EM-ThM12, 169; SE1-MoM4, 13; SE1-MoM5, **13**
Wong, S.S.: NS-WeA1, **151**
Woo, R.: NS+BI-MoA3, 28
Woo, S.H.: TF-ThP36, 229
Wood, B.: SS-ThP20, **223**
Woodall, S.: AS-FrM4, **232**
Woollam, J.A.: AS+EM+MS+TF-MoM3, **2**
Wooten, D.: EM-WeA11, 146
Wormeester, H.: AS+EM+MS+TF-MoM11, **3**
Worsely, M.: AS+NS-TuA1, 67
Wostenholme, J.: AS-TuP10, 90
Wright, A.E.: AS-FrM9, 233; AS-WeM10, **120**; EW-TuL3, 66
Wright, P.C.: BM+MN+MS+TF+BI-ThA10, 190; BM+MN+MS+TF+BI-ThA4, 190
Wrochem, F.: NS+BI-MoA6, 29
Wu, C.: SS2-MoM1, **17**
Wu, C.Y.: SE-MoA8, 31
Wu, D.: BI+AS+NS-FrM6, 234
Wu, K.J.: AS+NS-TuA1, 67
Wu, P.C.: BI+NS-MoM1, 4; NS-WeM9, **127**
Wu, P.S.: PS-ThP7, 217
Wu, R.Q.: MI+TF-ThA3, 194; SS1-TuM3, 58
Wu, W.: SS-TuP19, 113
Wu, Z.L.: SE2-MoM4, 14
Wüest, M.: VT-MoA1, **40**

— X —

Xia, J.-T.: BM-ThP1, 213
Xiang, C.X.: EM1+PV-TuM3, 47
Xiao, D.: MI+TF-ThA11, 195
Xiao, J.: BI+AS+NS-FrM6, 234
Xiao, Z.: EM-TuP21, 99; NS-TuP24, **104**
Xu, B.: SS2-ThM1, **182**
Xu, L.: PS2-ThM2, **179**
Xu, M.: EM-TuA3, 69
Xu, S.: NS-ThM1, 175; PS1-TuM11, 55
Xu, W.: IS+AS-ThA8, 193
Xu, Z.: SS1-TuM3, 58
Xue, J.: EM-WeM10, 123; PS2-TuM10, 57

— Y —

Yabutani, H.: NS+BI-MoA9, **29**
Yaffe, O.: NS1+PV-TuA11, 73
Yagi, T.: TF-ThP27, 228
Yakes, M.K.: EM-ThA2, **191**
Yamachika, R.: MI-FrM3, 236
Yamada, H.: AS-ThA8, 187
Yamada, T.: NS+BI-MoA9, 29; SS-ThP13, **222**
Yamaguchi, H.: SE1-MoM8, 13
Yamaguchi-Adams, Y.: PS1-TuM10, 54
Yamamoto, H.: PS-TuP7, **106**
Yamamoto, K.: PS1-MoM1, 9; PS-TuP7, 106
Yamamoto, S.: SS1-WeM4, 132
Yamashita, I.: PS-FrM10, 241
Yamashita, M.: MI-FrM9, **237**
Yamashita, S.: VT-WeM4, **139**
Yamazaki, K.: BI-TuP8, 95
Yamazui, H.: AS-WeA11, 143
Yan, M.: BI-ThP1, 210; BM-ThP3, 213; GR+TF-TuA11, **72**; GR-TuP2, 100; NS-TuP6, 101
Yan, X.-M.: MN-FrM9, 239
Yan, Y.: TF-ThA9, 208
Yang: MI-ThM2, 172
Yang, C.: EM-ThM11, 168; NS+BI-MoA9, 29
Yang, C.C.: NS-TuP26, 104
Yang, C.Y.: VT-WeA12, 163
Yang, D.: GR+TF-TuA10, 72
Yang, F.: EM1+PV-TuM3, 47; SS1-TuM9, **59**
Yang, H.: EM-TuP22, 99
Yang, J.: BI-MoA3, **25**; IJ+BI+MN+SE+AS-ThM9, 169; MN-ThP5, 215; NS-ThA7, **199**
Yang, J.C.: IS+AS-FrM2, **235**; SS1-TuM12, 59
Yang, K.: MI-ThM1, 172
Yang, L.: SS2-FrM9, 245
Yang, P.: BI-TuP5, **94**; NS+BI-MoA1, 28
Yang, S.P.: AS+NS-WeM12, 119
Yang, T.: SS2-ThA6, 206
Yang, W.: PS-ThP1, 216; SS2-ThA10, 207; TF-ThP13, **225**
Yang, X.Q.: IS+AS-ThA6, **193**
Yang, Y.: EM1+PV-TuM3, **47**; NS-WeM9, 127; PS2-ThM3, **179**; SS2-WeM3, 133; SS3-TuA4, **82**
Yang, Y.J.: PS-TuP14, 108; SE-MoA8, 31
Yang, Z.: IS+AS-ThA8, 193
Yanguas-Gil, A.: AS+EM+MS+TF-MoA8, **24**
Yano, K.: TF-ThP24, 227
Yarmoff, J.A.: NS+BI-MoM2, 7; SS1-FrM9, 243; SS1-TuM3, 58
Yasuda, A.: NS+BI-MoA6, 29; PS-TuA11, 76
Yatsuda, K.: PS2+MN-WeA4, 155
Ye, P.: EM-TuA3, 69
Yellen, B.B.: BI-ThP16, 212
Yeom, G.Y.: MI-ThP2, 214; PS1-TuM4, 53; PS2+PV-MoM2, 11; PS2-ThM5, 179; PS-ThP4, 217; PS-TuP11, 107; PS-TuP6, 106; SE-TuP4, 110; TF-ThP16, 226; TF-ThP25, 228; TF-ThP28, 228
Yeon, J.K.: PS1-TuM4, 53; PS-TuP6, 106
Yi, C.W.: SS1-MoM10, 17
Yi, W.: NS-TuP25, **104**
Yildirim-Ayan, E.: PS-FrM6, 240
Yim, C.J.: AS1-ThM12, 165
Yin, L.: MI+TF-ThA11, 195; MI+TF-ThA4, 194
Yin, W.: SS1-TuM5, **59**
Yin, Y.: PS1-MoM8, **10**
Yitamben, E.: MI+EM-WeA3, **150**
Yokota, Y.: AS-TuP7, **90**; SE-TuM6, 58
Yoo, J.-H.: EM-TuP24, **99**
Yoo, Y.-S.: PS1-WeM10, 129
Yoon, B.: TF2-TuA9, **85**
Yoon, D.: AS+EM+MS+TF-MoM9, 3
Yoon, J.H.: PS1-TuM1, 53
Yoon, J.J.: AS-TuP3, **89**
Yoon, K.H.: EM-TuP15, 98
Yoon, Y.-K.: MN-ThP5, 215; NS-TuP20, 103; NS-TuP22, 104
Yoshida, H.: VT-WeM11, **140**
Yoshida, N.: AS-TuP7, 90; SE-TuM6, 58; SS-ThP15, **222**
Yoshigoe, A.: AS-TuP9, 90
You, S.-J.: PS1-WeM10, 129
Young, E.W.A.: TF-FrM1, 246
Young, M.: TF-ThA9, 208
Young, T.: EM-WeM6, 122
Yu, C.C.: TF-ThP30, 229
Yu, C.S.: TF-ThP30, 229
Yu, G.P.: SE-TuP3, 110
Yu, H.: BI-ThP12, 211
Yu, K.M.: EM-ThA9, 192
Yu, L.: EM-TuA3, 69; EM-TuA4, 69; EM-TuA9, **70**
Yu, P.: EM2-TuM6, 49
Yu, S.: SS2-FrM3, 244
Yu, S.W.: MI+EM-WeA11, 151; MI-ThM6, 173
Yu, Z.Q.: IS+SS-ThM6, 171; SS3-TuA11, **83**
Yuan, X.: PS2+TF-WeM12, 131
Yubero, F.: AS-WeM5, **119**; SE+TF-TuA10, **78**; TF1-TuA7, 83
Yun, J.-G.: EM-TuP18, 98
Yuriy, P.: MN-ThP2, 215

— Z —

Zach, M.P.: MN+GR-ThM9, 174
Zahn, R.: TF2-MoA4, **38**
Zaidi, S.: TF-WeA9, 160
Zajec, B.: VT-WeA4, 163
Zakharov, A.A.: SS1+EM-MoA7, 32
Zalalutdinov, M.: MN-FrM4, 238
Zambelli, T.: TF2-MoA4, 38
Zander, N.: BI-MoA7, 26; BI-MoA8, **26**
Zandvliet, H.J.W.: EM-WeM5, 122
Zauscher, S.: AS2+BI-ThM5, **166**; BI+AS+NS-WeA10, 145; BI-ThP16, 212; BI-TuP10, 95
Zegenhagen, J.: SS2-ThA7, 206
Zehr, R.T.: SS2-MoM9, **18**
Zeinert, A.: EM-TuP2, 96; TF-WeA9, 160
Zepeda-Ruiz, L.: TF1-TuA10, 84
Zhang, C.: IS+AS-ThA9, 194
Zhang, F.: TF2-TuM5, 64; TF-WeM11, **136**
Zhang, J.G.: IS+AS-ThA8, 193
Zhang, J.-H.: BM-ThP1, 213
Zhang, K.: BI-ThP6, 210
Zhang, L.: TF1+PV-MoA10, 37
Zhang, P.: BI+NS-MoM2, 4; TF-WeA11, 160
Zhang, Q.: PS-ThP10, 218
Zhang, W.: SE+TF-TuA1, **76**
Zhang, X.: MI-FrM3, **236**; SS1-FrM1, 242; SS2-ThM12, 184
Zhang, Y.: PS1-ThM11, 178; SS2-MoA11, 35
Zhang, Z.: BI-MoA7, 26; IS+AS-FrM1, 235; PS2-TuM12, 57; SE+TF-TuA3, 77; SS2-MoM10, 18; SS2-MoM8, 18; SS2-WeM10, 134
Zhang, Z.Y.: MI+TF-ThA11, 195; SS1-ThA2, 204; SS2-TuM2, 60
Zhang, Z.Z.: BI+AS+NS-FrM6, **234**

Zhao, B.: TR+SE-WeA2, **161**
Zhao, H.: EM-TuA1, 69
Zhao, J.P.: PS2-ThM9, 180; PS-ThP17, **219**
Zhao, L.: AS-WeM9, 120
Zhao, X.: TR+SS-TuA7, 87
Zhao, Y.: AS-TuP5, 89; NS-TuP17, 103; SE+TF-TuA3, 77; TF1+SE-TuM3, 61
Zharnikov, M.: BI+AS+NS-ThA10, **189**; SS2-ThM5, 183
Zheng, J.: PS2+PV-MoM8, 12
Zheng, S.: EM-ThM2, 167
Zheng, W.: BI-TuM10, **46**
Zheng, Y.: EM-WeM10, 123
Zhinoviev, O.: NS-ThA1, 198
Zhitenev, N.B.: GR+MI-WeM12, 125; GR+MI-WeM5, 124; NS-ThA8, 199
Zhou, B.S.: PS-TuA3, 75
Zhou, D.: AS2+BI-ThM4, 166
Zhou, H.: TF-ThP33, **229**
Zhou, J.: NS-ThM1, 175; SS1-ThA8, **204**; SS2-WeM3, **133**
Zhou, K.: PS-TuP3, 106
Zhou, Q.: PS1-MoM9, **10**
Zhou, X.: EM-WeM1, 121
Zhou, Y.: PS-TuP3, **106**; SS1-ThA8, 204
Zhu, P.: NS+TR-TuM5, **53**
Zhu, W.G.: SS1-ThA2, 204; SS2-TuM2, 60
Zhu, X.: EN-WeA11, **147**
Zhu, Z.: AS-FrM6, 232; AS-FrM8, **233**; IS+SS-ThM6, 171; SS1-FrM10, 244
Ziemer, K.S.: VT-TuP5, 114
Zierold, R.: MI+TF-ThA9, 195
Zin, K.: PS1-MoM8, 10
Ziskind, D.: BI-ThP6, 210
Zoric, I.L.: SS2-MoA1, **33**
Zorn, G.: AS+NS-WeM4, **117**
Zubia, D.: EM2-TuM1, 48; TF1+PV-MoA1, 35
Zumer, M.: VT-WeA4, 163
Zuo, J.-M.: IS+AS-FrM5, **235**
Zwadlo, G.: TF3-MoA8, 40