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 $<\varepsilon>=<\varepsilon_1>+i<\varepsilon_2>$ 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 $<\varepsilon>$ 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.

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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.

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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.

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.

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 <u>during</u> irradiation have yielded vital information relevant to primary or initial electron-induced processes, analyzing the products <u>following</u> 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.

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, $E_0 + \Delta_0$, E_1, $E_1 + \Delta_1$, E_0', $E_0' + \Delta_0'$, E_2, and $E_2 + \Delta_2$ 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+Δ_2, E_2' and E_2' + Δ_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, $E_1 + \Delta_1$, E_0', $E_0' + \Delta_0'$, E_2, $E_2 + \Delta_2$, E_2', $E_2' + \Delta_2'$, 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, $E_2 + \Delta_2$, E_2', and $E_2' + \Delta_2'$ 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 $\Delta_5^{cu} - \Delta_5^{vu}$ and $\Delta_5^{cl} - \Delta_5^{vu}$ 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

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AS-TuP13 Investigation of Metal-Assisted SIMS and Cluster Ion Bombardment for Analysis of Polystyrene Surfaces

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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.

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AS-TuP14 Surface Analysis of Electro-Polished Niobium Cavity-Samples for RF Applications

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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.

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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.

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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 1.0×10^{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 $(SiH_3)_3P$ 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.

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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).

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.

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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.

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* 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.

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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.

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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.

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[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.

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:

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2 Dahlin, A. B.; Jonsson, M. P.; Höök, F. *Advanced Materials* **2008**, *20*, 1436-1442.

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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.

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

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* Paul Holloway Award Winner

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.

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.

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. $\lambda/30$). 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.

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.

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[1] Morrall P, Tull S, Glascott J, Roussel P, 2007 *J.Alloys Comp.* **444-445** 352.

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 signali ng 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.

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[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.

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) .

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.

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[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.

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