Monday Afternoon, October 20, 2008

Applied Surface Science
Room: 207 - Session AS-MoA

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

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

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

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

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

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

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

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

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

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

I will discuss two relatively new developments in photoemission: the use of nanometer-scale standing-wave (SW) excitation so as to selectively look at different depths below the surface[1-3] and the use of harder x-ray excitation in the multi-keV range so as to probe more deeply below the surface, in what has been termed HAXPES or HXPS.[4] Both of these approaches have the potential for enhancing the sensitivity of photoemission to both bulk and buried interface properties, while at the same time permitting the study of near-surface phenomena. After a brief overview of basic concepts, I will discuss several recent applications of these methods, separately and in concert. These will include: variable-temperature HXPS measurements at the ESRF on fractured cubic and cleaved bilayer lanthanum strontium manganite samples,[5,6] SW HXPS measurements at both BESSY[7] and SPring8[8] on systems of relevance to spintronic and semiconductor IC applications, the possibility of doing angle-resolved HXPS so as to carry out band mapping,[9] and the possible benefits of photoelectron diffraction in the hard x-ray regime for local structure determinations.[10]

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

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

[2] S.-H. Yang, B.S. Mun, and C.S. Fadley, Synchrotron Radiation News 17 (3), 24 (2004).

[3] S.-H. Yang, B. S. Mun et al., J. Phys.: Condens. Matter 18, L259–L267 (2006).

[4] C. S. Fadley, Nucl. Inst. and Meth. A 547, 24-41 (2005), and other papers in this special journal issue edited by J. Zegenhagen and C. Kunz.

[5] F. Offi et al., Phys. Rev. B 75, 014422 (2007).

[6] F. Offi, N. Mannella et al., Phys. Rev. B, in press.

[7] F. Kronast, S. Döring, M. Gorgoi, R. Ovsyannikov, A. Kaiser, C. Wiemann, S.-H. Yang, M. Huijben, A. Locatelli, D. E. Bürgler, R. Schreiber, F. Schäfers, W. Braun, H.A. Dűrr, C. M. Schneider, C. Westphal, C. S. Fadley, BESSY Highlight 2007, and to be published.

[8] C. Papp, B. Balke, et al., to be published.

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

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

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

Fast parallel XPS imaging of surfaces has been commercially available for more than a decade. During this time numerous examples of both elemental and chemical state images have been published. X-ray photoelectron imaging has become a routine technique for the determination of lateral distribution of elements and chemical species at the surface and capable of a lateral resolution of <3µm over areas of several millimetres. More recently the spherical mirror analyser (SMA), used for energy selection in XPS imaging applications, has been combined with the delay line detector (DLD), a two-dimensional, pulse counting electron detector. This detector has allowed the realisation of quantitative surface chemical state microscopy by XPS. To generate such information requires the acquisition of a several images, or a series of images, incremented in energy so that each pixel contains photoelectron intensity information as a function of photoelectron energy. Fast counting electronics enable the detector to collect over 65,500 pixels per image. The different methods of collecting the necessary data and the application of multivariate analysis to analyse the information content of the data and as a tool for noise reduction in individual images or spectra will be described. Methods for obtaining the maximum information from the minimum acquisition time will also be discussed. The application of the various approaches to a variety of diverse samples will be presented.

5:00pm **AS-MoA10 Structural Properties of Epitaxial SrHfO$_3$ Thin Films on Si(100)**, ***M. Sawkar-Mathur***, University of California, Los Angeles, *C. Marchiori, J. Fompeyrine,* IBM Zurich Research Laboratory, *J. Bargar, M. Toney,* Stanford Synchrotron Radiation Laboratory, *J.P. Chang*, University of California, Los Angeles

Hafnium based amorphous oxides are currently being implemented to enable the 45-nm and 32-nm technology nodes of metal oxide semiconductor field effect transistors (MOSFETs). However, the interfacial issues arising at the amorphous oxide/crystalline Si interface justify the exploration of a lattice-matched crystalline oxide on Si to achieve an atomically sharp interface, thereby improving the device reliability. In this work, SrHfO$_3$, a perovskite oxide, was grown on silicon using molecular beam epitaxy (MBE). In-depth structural analysis using synchrotron techniques including XRD with a four circle diffractometer and grazing incidence EXAFS was performed to determine the crystalline quality and short range chemical bonding and order in these ultra-thin SrHfO$_3$ films. Nearly epitaxial growth of SrHfO$_3$ on Si was observed with good crystalline quality and some misalignment of grains. From the in-plane diffraction pattern, the SrHfO$_3$ (100) plane was found to be parallel to the Si(110) plane, yielding a 6% lattice mismatch. The d spacing of the SrHfO$_3$ (300) plane was found to be 1.37 Å which corresponds well with the literature reported value of 1.36 Å, suggesting no significant strain in the film. Phi scans of the SrHfO$_3$ (200) peak showed the four-fold symmetry expected for that plane, with no twinning, further substantiating the lack of significant strain in the film. The atomic planes were found to be highly parallel, as evidenced by the presence of interference fringes around the SrHfO$_3$ (001) plane. Cluster models with a radial distance of 4 Å were constructed using the perovskite crystal structure of SrHfO$_3$ to model the scattering amplitudes of the absorption spectra and quantify the nearest and second nearest neighbors surrounding the center absorbing Hf atom. A low level of disorder and minimal defects were observed. Based on the complementary analyses of synchrotron GI-EXAFS and XRD, MBE grown SrHfO$_3$ on Si has the potential to be a crystalline metal oxide for implementation in CMOS devices.

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

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

Applied Surface Science
Room: 207 - Session AS-TuM

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Applied Surface Science
Room: 207 - Session AS-TuA

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

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

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

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

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

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

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

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

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

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

3:00pm **AS-TuA5 Work Function Measurements of W-based Metal Gates by Ultraviolet Photoelectron Spectroscopy and Kelvin Force Microscopy**, ***E. Martinez***, *F. Pierre, D. Mariolle, N. Benedetto, J.P. Barnes, R. Gassilloud, O. Renault, F. Martin, F. Bertin, A. Chabli, N. Chevalier*, CEA-LETI, France

The scaling of metal-oxide-semiconductor devices faces the challenge of metal gate integration to replace poly Silicon metallization. These metal gates will provide lower electrical resistivity and thinner EOT by removing depletion. New materials based on tungsten alloys are being investigated because of high thermal stability and corrosion resistance. W and WSi are good candidates because of a middle-gap work function that is shifted to P+ or N+ by ion implantation. Before integration in sub-45 nm nodes, the effective work function of the metal gate must be accurately evaluated. Complementary surfaces characterization techniques such as Kelvin Force Microscopy (KFM) and Ultraviolet Photoelectron Spectroscopy (UPS) can be used. Due to extreme surface sensitivity, surface preparation is mandatory before carrying out the measurements. Auger and TOF-SIMS depth profiles evidence the presence of native tungsten and silicon oxides on top of W and WSi materials, respectively. Removal of these oxides must be performed before KFM or UPS measurements, in order to estimate the real metal work function. We investigate here the impact of surface treatments, such as chemical etching, ion sputtering, and thermal annealing on the work function measurement. For WSi metal gates, HF based chemical etching is used to partially remove SiO2. For W metal gates, annealing at 700°C is performed to evaporate WO3. Subsequent X-ray Photoelectron Spectroscopy (XPS) is carried out to follow the evolution of the chemical surface composition. A detailed analysis of Si2p and W4f core levels evidences partial removal of native oxides. Gentle argon sputtering is finally performed to fully remove the superficial oxide. UPS and KFM measurements are performed after these surface treatments. A crossed study of the results obtained by these techniques will be commented. AFM and SEM results will highlight the roughness and morphology of the surface after each surface treatment.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Plasma-deposited Polymer and Organic Surfaces in Biological Applications

Moderator: E.R. Fisher, Colorado State University

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

In the search for new and improved biomaterials, combinatorial material discovery approaches are increasingly being explored. A significant development in the production of polymer libraries by parallel synthesis was the move from preparation of macroscopic samples,[1] to on-slide polymerisation as microarrays in nano-litre volumes.[2] Such microarray material libraries may readily be interrogated by automated surface analysis equipment. Recently, high throughput surface analysis of a library of 576 different acrylate copolymers in triplicate on one slide using water contact angle (WCA), XPS and ToF SIMS highlighted the difference in the bulk and surface composition of the polymer spots, and consequently the need for surface analysis data when determining structure-property relationships.[3] The complexity of SIMS data, multiplied by the number of different samples necessitates the use of multivariate analytical approaches. Using partial least squares (PLS) analysis, relationships between SIMS fragments and WCA have led to identification of moieties controlling wettability across the wide range of copolymers synthesised on one microarray.[4] Comparison of human embryonic stem cell number on the spots with SIMS spectra have identified further SIMS fragments that correlate with high or low cell-polymer affinity. Protein adsorption measurements have been undertaken in an attempt to rationalise the cell adhesion data.[5] The correlations identified, and the information on the relationship between the surface structure and cell response or wettability will be discussed in this exploration of the high throughput approach.

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

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

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

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

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

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

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

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

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

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

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

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

In the course of our research how deposition conditions teleologically influence the morphology and various physical properties of the surface of various derivates of parylene, we followed the Yasuda approach to correlate the deposition rate of polymeric films with external parameters (flow rate and power) to define three different regimes of growth.[1,2] Since external parameters, especially the pressure, influence the polymerization in an opposite manner (rising the pressure causes an increase in the collision rate, but a decrease in electron temperature) we studied the deposition of parylene vapors with and without pulsed microwave plasmas to correlate outcome parameters such as surface energy, roughness, and deposition rate with respect to plasma density and electron temperature (Langmuir and OES) by varying the molar fraction of the monomeric species, diluted by the noble gas argon, the total pressure and the power. For this end, we determined the vapor pressure of the dimer and the chemical equilibrium between the monomer and the dimer by varying the evaporation temperature and the cracking temperature, resp., and cross-checked this equilibrium by mass spectrometry. This method has been extended to explain the onset of volume polymerization which becomes manifest by slight tarnishing of the polymer. Following Yasuda, this happens when a certain ratio of number density of the monomeric species to plasma density is exceeded. After having established stable process windows, two further tracks have been followed, namely copolymerization with CF_4 (volume polymerization) and hydrophilic functionalization. Following Gogolides, the surface roughness has been correlated to contact angle measurements.[3] The super-hydrophobic character is mainly due to surface roughening (nanotexturing) in the case of normal CVD. However, plasma treatment leads to super-hydrophobic character also for smooth surfaces. Subsequent treatment with O_2 generates long-term stable hydrophilic surfaces. To calibrate the effect of momentum transfer and to separate the chemical effect of etching, this has been compared with Ar etching.

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

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

[3] A.D. Tserepi, M.-E. Vlachopoulou, and E. Gogolides; Nanotechnology 17, 3977 (2006).

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

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

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

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

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

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

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

Tuesday Afternoon Poster Sessions

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

Aspects of Surface Analysis Poster Session

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

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

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

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

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

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

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

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

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

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

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

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

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

AS-TuP7 XPS Analysis of a Complex Metal Oxide Coatings on Stainless Steel: Depth Profiling, ***H.M. Meyer, III***, Oak Ridge National Laboratory

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

AS-TuP8 Structural Characterization of Ag Nanoparticles Embedded in TiO$_2$ Thin Films Prepared by Means of RF-Magnetron Sputtering, ***V. Moellmann***, University of Paderborn, Germany, *P. Keil, J. Zuo, H. Itani, T. Titz,* Max-Planck-Institut fuer Eisenforschung GmbH, Germany, *G. Grundmeier*, University of Paderborn, Germany

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

AS-TuP9 Deposition and Characterization of Aluminum Oxynitride Optical Coatings, ***Y. Liu***, *N. Gunda, R. Cooke, R. Raman*, Entegris Inc.

Aluminum oxynitride (AlON) has received extensive attention due to its composition-dependent tunability in mechanical and optical properties. Aluminum oxynitride has been identified as a potential candidate material to replace sapphire (single crystal aluminum oxide) in various optical applications. However, it is still relatively expensive to fabricate bulk AlON by the conventional ceramic processing technique. The cubic AlON phase in the bulk material is obtained by a high temperature-synthesizing process to retain the crystal structure, which gives it optical, IR transparency and other attractive properties. It would be of importance for a number of applications, if the benefits of AlON properties could also be achieved in thin films. This thin film could then be applied on a variety of base substrates cost effectively. In this work, aluminum oxynitride coatings were deposited by magnetron sputtering followed by thermal treatments at different temperatures to evaluate phase conversions. Microstructures and phase constitution of both as-deposited and thermally treated AlON coatings were characterized by scanning electron microscopy (SEM), atomic force microscopy (AFM) and grazing incidence X-ray diffraction (GID). X-ray photoelectron spectroscopy (XPS) was employed to study the AlON coatings with respect to the stoichiometric composition and atomic bonding states. Mechanical properties such as Young's modulus, hardness and coefficient of friction of AlON coatings were investigated by depth-sensing nano-indentation and nano-scratching experiments. Optical properties of AlON coatings were examined by measuring refractive index, reflectance and transmittance in both visible and infrared range. The mechanical and optical properties of AlON coatings were compared with the powder-processed AlON ceramics.

AS-TuP10 Quantitative Analysis of Si-Ge Alloy Films and Compositional Depth Profiling of Si/Ge Multi Layers Using SIMS, *K.J. Kim,* ***J.S. Jang,*** Korea Research Institute of Standards and Science, *T.E. Hong,* Korea Basic Science Institute, *H.J. Kang*, Chungbuk National University, Korea

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

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AS-TuP11 Quantitative Multi-Technique Analysis of Silicon Germanium Semiconductors, ***R.E. Davis***, *M. Hatzistergos, B.M. St. Lawrence, T.L. Tai, A.G. Domenicucci, A Madan, T.L. Pinto, P. Ronsheim, Z. Zhu, A.R. Turansky, J.R. Holt, M. Hopstaken, T.N. Adam*, IBM Corp.

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

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

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

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

AS-TuP12 Atmospheric Plasma Surface Modification Analysis by Energy Resolved Molecular Beam Mass Spectrometry and SIMS, ***P.J. Hatton****, Y. Aranda Gonzalvo, G.A. Cooke, T.D. Whitmore, D.L. Seymour, C.L. Greenwood, J.A. Rees*, Hiden Analytical, UK

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

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

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

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

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

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

AS-TuP16 Effect of Polymer MW on XPS Valence Band Spectra, ***J.L. Fenton****, J. Chen*, The Dow Chemical Company

The molecular weight of a polymer can alter the properties of films as low molecular weight components migrate to the polymer surface. XPS (x-ray photoelectron spectroscopy) is an ideal method to characterize the surface for the presence of low molecular weight polymers. XPS valance band spectra have been shown to be an excellent method to quantify the amount of propylene or ethylene at the surface of ethylene-propylene blends. Valance band spectra can also be used to detect changes due to secondary structure. The work presented here shows how XPS can identify the changes in the valance band due to MW.

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

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

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

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

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

A giant cluster ion impact method, electrospray droplet impact (EDI) ionization, has been developed for matrix-free secondary ion mass spectrometry.[1] EDI utilizes the electrospray charged water droplet as the extremely high-momentum projectiles. The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure are passed through an orifice into the vacuum chamber, transported into a quadrupole ion guide, accelerated by 10kV after exiting the ion guide and impact on a target. Roughly, the charged water droplets may be represented as $[(H_2O)_{90000}+100H]^{100+}$ with mass of~$1.6\text{x}10^6$ u. The kinetic energy of impacting projectile is ~10^6 eV.[2] The polymer samples (PET, PMMA, PS) etched by EDI were evaluated by X-Ray Photoelectron Spectrometer (XPS: JEOL JPS-9200). A comparative study for PET, PMMA and PS etched by

Ar^+ ion and EDI was made. For the surfaces of PET, PMMA and PS etched by Ar^+ ion, the deoxygenation and graphitization were found. The degradations of the polymers by the ion sputtering are slightly suppressed by using the low energy ion or the cluster ion. But, the effect of suppressing degradations was depended on the polymers. On the other hand, the deoxygenation, and graphitization were not observed on the surfaces of PET, PMMA and PS etched by EDI. It supposed that the kinetic energy of impinging water droplet at the moment of impact on the target by EDI is efficiently converted to the internal energies of water molecules in the selvedge of the colliding interface. The rest is dissipated as shock waves propagating through the target and the water droplet. This verifies that EDI is capable of no degradations of the polymer surface etching. The other experimental results of EDI applied to metals, semiconductors will be given. Acknowledgement: This work was supported by the Japan Science and Technology Agency.

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

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

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AS-TuP21 Analysis of DLC Fine Structure on Sliders by Using Second Derivative Carbon KLL Auger Spectra, ***K.W. Wierman***, *F.Y. Chen*, Seagate Technology

Present hard disc drive (HDD) manufacturing technology uses diamond-like carbon films (DLC) as overcoats for both head and media. These DLC films function to protect underlying magnetic metals from wear and corrosion both during the manufacturing process and throughout the design lifetime of the drive. Recording head DLC film thickness can vary from ~15 to ~30 Å while typical values of DLC films for magnetic media are in excess of 30 Å. Auger analysis is particularly suitable for overcoat studies due to the surface sensitivity of the technique. In this study an Omicron high resolution Auger/SEM system was utilized to investigate the DLC at the head air bearing surface. Carbon's Auger spectrum is particularly sensitive to the type of bond hybridization.[1] Graphite, diamond, and silicon carbide have distinctive Auger CKLL spectra and its fine structure that can be used to identify the form of carbon at the surface. A second derivative of the Auger spectrum was utilized to remove the background and highlight the carbon fine structure peak locations (maximum negative curvature).[2] To remove the surface hydrocarbons a 15 second 0.3keV Ar etch was utilized. W. Zhu et. al. showed that by reducing the Ar beam energy to 0.3keV and limiting the total flux to 1.0×10^{14} ions/cm^2 an effective cleaning of hydrocarbon contaminates from the surface of CVD diamond films was accomplished without negatively impacting the diamond carbon bond structures.[3] In-situ XPS data on DLC grown films on coupons was also completed for comparison of the carbon bond structure.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Applied Surface Science
Room: 207 - Session AS-WeM

Advanced Data Analysis for Surface Characterization
Moderator: S. Pachuta, 3M

8:00am **AS-WeM1 Near Real-time Analysis of XPS Data**, *A.S. Lea, D.R. Sisk, M.H. Engelhard,* Pacific Northwest National Laboratory, *J.E. Castle,* University of Surrey, UK, *D.R. Baer*, Pacific Northwest National Laboratory

The application of x-ray photoelectron spectroscopy (XPS) to analyze different types of materials appears to be growing rapidly around the world. In our Department of Energy National User Facility the Environmental Molecular Sciences Laboratory (EMSL) we currently have user requests for thousands of hours per year of XPS based experiments and more routine sample analysis. The real-time (or near real-time) analysis of the XPS data as it is collected has significant potential advantages to scientists and instrument operators in that it has the potential to qualitatively alter the way experiments are done. Such endeavors have the potential, not only to improve the turn-around time for data analysis and the sophistication of data analysis reportable to the User, but also to reduce the labor involved in data analysis, resulting in significant time (and cost) savings. We are developing a prototypical real–time data analysis capability to analyze x-ray photoelectron spectroscopy (XPS) data generated in EMSL. Our goals are to provide atomic composition, carbon contamination layer thickness and component segregation (layer) information as soon as adequate data is collected on a specimen. Because of the high user need and previous efforts to design an XPS expert system, XPS is a good candidate for development of a near real time data analysis capability. Our real-time data analysis package follows many elements of the expert system approach proposed by Castle.[1] A set of rules and algorithms are used to address a well defined series of analysis objectives (based on the needs of the XPS analysis) to characterize the surface in terms of atomic concentration, layer sequences, and enrichment/depletion of elements as a function of depth. For each goal, rules have been developed to determine whether the stated goals are met. The real-time analysis package evaluates the rules by automated interpretation of the wide-scan (survey) spectra. Once the goals have been met, the real-time analysis package generates a report that includes, in addition to the above stated goals: a first level approximation of surface composition and metadata associated with this analysis, which will be stored with the datafile produced by the data analysis package.

[1] Castle, J.E., J. Vac. Sci. Technol. A (2007) 25, 1-27.

8:20am **AS-WeM2 Data Scaling for Quantitative Imaging XPS**, *J. Walton,* The University of Manchester, UK, *N. Fairley*, Casa Software

Multivariate analytical techniques are seeing increasing use in surface analysis due to the ability of current instrumentation to acquire multispectral data sets. Their use can provide a significant improvement in signal/noise, and simplify analysis of the large amount of data present by reducing its dimensionality. In the case of XPS this enables quantification by measurement of photoelectron peak areas, and chemical state determination using curve fitting to the spectrum at every pixel in an image. Selection of the most appropriate technique is dependent upon the characteristics of the data, and for XPS, where there are relatively few components compared with the number of objects in the data set, Non-linear Iterative Partial Least Squares (NIPALS) affords a significant saving in computational requirements, as the procedure may be terminated after the appropriate number of components has been calculated. A key aspect in the use of these techniques is their ability to order the data so that the chemical information is easily separated from the noise. For data acquired by pulse counting, which is governed by Poisssonian statistics and where the variance scales as the data, ordering the data by variance may result in noise from high intensity photoelectron peaks dominating low intensity chemical information. Effective separation of noise and chemical information therefore necessitates prescaling the data, so that the noise is evenly distributed. Individual objects, whether images or spectra, may be scaled by the square root of the variance. This provides good separation of the chemical information from the noise, but leads to a signal level below which information cannot be extracted. This is not important where the inelastic background is greater than this base level, but leads to significant errors in quantification where the background is equal to, or below this level, and data is lost from photoelectron peaks. This is particularly important for photoelectron peaks occurring at low binding energy. It will be shown that scaling to the square root of the mean variance in both image and spectral domains, known as optimal scaling, avoids this limitation and allows use of the NIPALS procedure for fully quantitative imaging XPS.

8:40am **AS-WeM3 Using Multivariate Analysis and Modeling for Structure-to-Property Relationships Built from XPS Data**, ***K. Artyushkova***, *J.E. Fulghum, P. Atanassov*, The University of New Mexico **INVITED**

This talk will discuss new approaches in accelerating material development and design by building models describing structure-to-property relationship based on X-ray Photoelectron data. The science of designing of heterogeneous materials has benefited from an understanding of the chemical, surface and materials phenomena at the nanoscale. Among the more complex nano-structured functional materials that will be discussed in this talk are electrocatalysts and biocatalysts. Understanding the structure of catalysts, and linking this structure to performance is essential for identification of the active catalytic sites, for optimization of catalyst performance, and elucidation of failure mechanisms. XPS is one of the most widely utilized surface spectroscopic techniques for analysis of catalyst structure. The ability to discriminate between different surface oxidation states and chemical environments is one of the primary advantages of the use of XPS in the characterization of catalyst structures. It is critical that the XPS spectra are interpreted and quantified with a high confidence level, as this information will be a central link between structure and performance. Although, the majority of XPS analyses of catalysts are focused on identifying the oxidation state and overall speciation, the ambiguity in peak assignment from overlapping peak components in XPS spectra is still a significant problem. Multivariate statistical methods of data analysis (MVA) are of critical importance in developing unambiguous methods of XPS data interpretation. Correlation of XPS structural data to any other property, such as derived from BET porosity, microscopic images and performance characteristics, represents a multivariate problem. Initially, Principal Component Analysis and Correlation maps will be used to study qualitative correlations between amounts of chemical species detected by XPS and variety of relevant for particular system macroscopic properties such as surface area, pore size distribution, electrochemical performance, corrosion rate, etc. In order to learn about relationship between several independent variables and a dependent variable and to determine the magnitude of those relationships, a variety of Regression Models are widely used. Multiple Linear Regression along with Genetic Algorithm for Variable selection will be discussed in attempt to build a predictive model between XPS, macroscopic parameters and performance characteristics.

9:20am **AS-WeM5 Identification and Quantification of ToF-SIMS Images with Topography using Multivariate Analysis**, ***J.L.S. Lee***, *I.S. Gilmore,* National Physical Laboratory, UK, *I.W. Fletcher,* Intertek MSG, UK, *M.P. Seah*, National Physical Laboratory, UK

Surface topography is a crucial issue for the analysis of many innovative devices such as microfluidic systems, fibres, composite materials, sensors, organic electronics and biomedical devices. The strength and durability of these components is critically dependent on their nanoscale surface chemistry and molecular interactions. However, quantitative characterisation of surfaces with topography remains a significant challenge due to the lack of systematic and validated measurement and data analysis methods. Previously, we presented a systematic study of the effects of surface topography on ToF-SIMS and provided guidance to practical analysts for identifying and reducing topographical effects.[1] Here, we investigate the robust use of multivariate methods for the identification and quantification of ToF-SIMS images with surface topography using principal component analysis (PCA) and multivariate curve resolution (MCR). Multivariate analysis simplifies the description of data and is powerful for identifying trends and highlighting chemically significant areas on images. However, many challenges remain with its application to complex images obtained in practical analysis, especially where sample topography or detector saturation[2] gives rise to large non-linear intensity variations in the data. In this study, we use several model samples, including polymer fibres with multi-organic coatings, natural starch grains and human hair, to investigate the merits of different multivariate analysis strategies for samples with topography. The emphasis is placed on the accurate identification and quantification of surface chemistry using careful application of multivariate methods, combined with suitable data selection and preprocessing and valid interpretation of the results. This study extends from our previous work on flat samples[3] and provides helpful guidance in the rapid, unbiased analysis of high-resolution raw spectral data in ToF-SIMS images of increasingly complex multi-organic surfaces and biomaterials.

[1] J L S Lee, I S Gilmore and M P Seah, Appl. Surf. Sci. in press

[2] M R Keenan, V S Smentkowski, J A Ohlhausen and P G Kotula, Surf. Interface Anal. 40 (2008) 97-106

[3] J L S Lee, I S Gilmore and M P Seah, Surf. Interface Anal. 40 (2008) 1-14.

9:40am **AS-WeM6 Methods for Reducing Topographical Influences in ToF-SIMS Spectral Images**, ***J.A. Ohlhausen***, *M.R. Keenan*, Sandia National Laboratories

Time-of-Flight Secondary Ion Mass Spectrometry is used to analyze surfaces and surface volumes of many kinds of materials. Many times the surfaces are rough in texture and contain variable materials compositions, thus affecting secondary ion responses. Data interpretation can be influenced unknowingly by topographical differences that might be present. In 3D analysis, data are typically represented as idealized cubes. Actual data will vary from the ideal cube in some unknown way. Spatial distortion from the idealized cube can be caused by several events including starting topography and differential sputtering rates. By understanding morphological and sputtering deviations, a 3D profile can be adjusted to reflect the actual shape of the removed volume. Strategies for measuring topographies and correcting images for 2D and 3D analysis will be presented. Pitfalls and shortcomings will be discussed.

Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

10:40am **AS-WeM9 The Effects of Pre-Processing of Secondary Ion Mass Spectrometry (SIMS) Image Data on Self-Modeling Image Analysis**, ***W. Windig***, *B.M. Wise*, Eigenvector Research, Inc., *M.R. Keenan*, Sandia National Laboratories

SIMS imaging is a powerful technique for surface analysis. The data from SIMS results in hundreds or thousands of images corresponding to ions of different masses. In order to facilitate data analysis, data reduction techniques are required. One of the tools to reduce the massive amounts of data is self-modeling mixture analysis, which expresses the SIMS image data in a few images representing pure components and their associated mass spectra. This paper will focus on the pure variable approach. A pure variable has contributions from only one component in the mixture data set (i.e. a value of m/e to which only one chemical component contributes) and thus can be used as a relative concentration estimate to resolve the mixture data into pure component spectra and their contributions ("concentrations') in the form of images. Similarly, pure pixels can be selected to resolve the mixture data. Image data are often of a noisy nature. Therefore, pre-processing of the data is often used to improve the results. A popular pre-processing for TOF-SIMS data is based on the Poisson nature of the data. This paper will show a modification of Poisson scaling procedure of the data, which makes it less susceptible to noise. Another way to enhance data analysis is using correlation based techniques to minimize the influence of outlying pixels. This paper will show how the data analysis results, as obtained with the pure variable/pixel approach, can be improved using the proper pre-processing tools, using data sets of actual samples of several chemical mixtures and a fused metal sample.

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11:00am **AS-WeM10 Comparison of MAF and PCA for Processing 3-D ToF-SIMS Images of Organic and Biological Samples**, ***B.J. Tyler***, University of the West Indies, Trinidad and Tobago

Recent technological advances have facilitated 3-D SIMS imaging of organic and biological samples. To fully realize the potential of this technology, new tools are needed to aid in the image analysis. Even in two-dimensions, obtaining clear contrast between chemically similar regions, distinguishing between chemical and topographical effects and identifying chemical species from a complex ToF-SIMS data set can be a formidable challenge. These challenges become even greater as the size and complexity of the data sets increase due to both the third dimension and the higher useful mass range commonly obtained with cluster ion sources. In the past, we have found that Maximum Autocorrelation Factors (MAF) provides significant improvement over PCA for enhancing image contrast, reducing spectral complexity and facilitating compound identification.[1,2] We have investigated several approaches to generalizing the MAF approach for use in 3 dimensions. These 3-D MAF algorithms have been tested on synthetic images and on a variety of organic and biological 3-D SIMS images. Results have been compared to converntion single-peak data analysis and to PCA results using various scaling options. MAF, which includes information on the nearest neighbors to each pixel, shows clear advantages over PCA, particularly for identifying spase of subtle components in the images. Additionally, MAF is insensitive to pre-processing choices that can dramatically influence PCA results.

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[1] Tyler, B.J. Applied Surface Science, Volume 252, Issue 19,30 July 2006, Pages 6875-6882

[2] Tyler, B.J.,Rayal G, Castner D.G., Biomaterials 2007, May 28(15):2412-23.

11:20am **AS-WeM11 SVD + Factor Rotation: A Powerful Alternative to PCA for Spectral Image Analysis**, ***M.R. Keenan***, Sandia National Laboratories

Factor analysis has proven an effective approach for distilling high dimensional spectral-image data into a limited number of components that describe the spatial and spectral characteristics of the imaged sample. Principal Component Analysis (PCA) is the most commonly used factor analysis tool; however, PCA constrains both the spectral and abundance factors to be orthogonal, and forces the components to serially maximize the variance that each accounts for. Neither constraint has any basis in physical reality; thus, principal components are abstract and not easily interpreted. The mathematical properties of PCA scores and loadings also differ subtly, which has implications for how they can be used in abstract factor "rotation" procedures such as Varimax. The Singular Value Decomposition (SVD) is a mathematical technique that is frequently used to compute PCA. In this talk, we will argue that SVD itself provides a more flexible framework for spectral image analysis since spatial-domain and spectral-domain singular vectors are treated in a symmetrical fashion. We will also show that applying an abstract rotation in our choice of either the spatial or spectral domain relaxes the orthogonality requirement in the complementary domain. For instance, samples are often approximately orthogonal in a spatial sense, that is, they consist of relatively discrete chemical phases. In such cases, rotating the singular vectors in a way designed to maximize the simplicity of the spatial representation yields physically acceptable and readily interpretable estimates of the pure-component spectra. This talk will demonstrate that this approach can achieve excellent results for difficult-to-analyze data sets obtained by a variety of spectroscopic imaging techniques. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

11:40am **AS-WeM12 A Comparison of Multivariate Statistical Analysis Protocols for ToF-SIMS Spectral Images**, ***V.S. Smentkowski***, *S.G. Ostrowski*, General Electric Global Research Center, *M.R. Keenan*, Sandia National Laboratories

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) instruments produce raw data sets with a tremendous quantity of data. Multivariate Statistical Analysis (MVSA) tools are being used to boil the massive amount of chemical information into a smaller set of components which are easier to interpret and understand due to species association. Standard Principal Component analysis (PCA) is the most heavily used MVSA algorithm used in the ToF-SIMS community. Other algorithms such as Multivariate Curve Resolution (MCR) have also gained popularity over the past few years. In this work, we compare the as-measured ToF-SIMS spectrum and ion images with four MVSA data analysis protocols; standard PCA, image-rotated PCA, spectra-rotated PCA, and MCR. Image-rotated PCA and spectra-rotated PCA are variations of standard PCA that involve abstract rotation of the principal components, and are designed to enhance either spatial contrast or spectral contrast in the components, respectively. We will show that the four MVSA protocols provide essentially the same information, but accentuate different aspects of the sample's composition and lateral distribution, and that taken together these methods provide a more complete understanding of the sample. We will demonstrate that the component spectra provided by MVSA protocols assists the analyst in understanding species correlation which would have been difficult, if not impossible, using univariate analysis protocols. Since each component image is represented by an associated spectrum (and not just a single peak) enhanced signal-to-noise and contrast is obtained. For the data set described here, MVSA tools identified unexpected species, which were not obvious in the as measured data.

Biological, Organic, and Soft Materials Focus Topic
Room: 201 - Session BO+AS+BI+NC-WeM

Organized and Structured Organic Interfaces
Moderator: J.S. Shumaker-Parry, University of Utah

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

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

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

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

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

Bis(terpyridine)derivatives (BTP) form highly ordered hydrogen bonded 2D networks on graphite (HOPG) at both the solid/liquid[1,2] and the solid/gas[3,4] interface. As found by STM at both interfaces, these adlayer structures depend on the positions of the N-atoms within the molecules, which can be varied via the synthesis process.[1,2] Complementary to the STM studies, we have performed temperature programmed desorption experiments of two different types of BTP molecules on HOPG. This revealed quantitative insights into phase stabilities of 2D (monolayer) and 3D (multilayer) phases. As to be expected from their large mass (618 amu) and correspondingly large moment of inertia, the translational and rotational degrees of freedom are found to play an important, even dominant role for the stability of more or less densely packed phases. This becomes apparent in strongly differing pre-exponential factors for desorption out of 2D and 3D phases. In agreement with STM observations at 300 K, the most stable phase (i.e., the one with the lowest chemical potential) for both molecules is not a close packed hydrogen bonded one, but a dilute 2D gas with facilitated translation and planar rotation. In this picture, ordered, hydrogen bonded structures observed at room temperature are only stabilized by the strong molecule-substrate interaction that allows enforcing higher coverages that go along with the more densely packed, ordered structures.

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

Applied Surface Science
Room: 207 - Session AS-WeA

Frontiers of Analysis and Combined Materials
Moderator: D.J. Gaspar, Pacific Northwest National Laboratory

1:40pm **AS-WeA1 Ambient Surface Mass Spectrometry – DESI – Towards a Metrological Framework**, *F.M. Green,* National Physical Laboratory, UK*, P. Stokes, G. O'Connor,* LGC Ltd., UK*, **I.S. Gilmore***, National Physical Laboratory, UK **INVITED**

There has been an explosion in the growth of ambient surface mass spectrometries with new ionisation and desorption methods developing rapidly. Surface chemical analytical techniques such as SIMS are extremely powerful providing high-sensitivity molecular information at better than 200 nm spatial resolution. However, the requirement for analysis in vacuo is for many applications a severe drawback. This is, of course, particularly important in biology. In the vanguard of these ambient methods is Desorption Electrospray Surface Ionisation (DESI) developed by the Cooks group.[1,2] DESI has already been shown to have great potential in a wide range of application areas from forensics and homeland security, through to counterfeit detection of pharmaceuticals and biological analysis. Of the wide variety of desorption methods it is clear that DESI has one of the strongest uptakes and so it is with DESI that we begin the development of a metrological approach, similar to that developed for SIMS and XPS. The objective is to improve repeatability and reproducibility and consequently confidence in the method and uptake into industry. A first step in the development of a metrological framework is to measure and improve repeatability. Here we conduct a systematic study of the parameters affecting spectral intensities and the interaction of the electrospray jet with the material surface. We have developed a well-controlled model system of Rhodamine B on glass that allows the effect of key experimental parameters such as geometry and spray conditions to be studied and optimised. Using this approach we have improved the repeatability of spectral intensities to 20%. In addition, we have studied the surface crater and surrounding disrupted material which gives insights into the interaction mechanism of the electrospray jet and the surface. This is important to allow future improvements in resolution and to understand the rate at which material is removed.

[1] Z. Takats, J. Wiseman, B. Gologan, G. Cooks; Science, 306 (2004) 471

[2] G. Cooks, Z. Ouyang, Z. Takats, J. Wiseman, Science, 311 (2006) 1566.

2:20pm **AS-WeA3 Shallow-Depth Surface Etching by Electrospray Droplet Impact**, ***K. Hiraoka****, Y. Sakai, D. Asakawa,* University of Yamanashi, Japan*, Y. Iijima*, JEOL Ltd.

A new ionization method, electrospray droplet impact (EDI) ionization, has been developed for matrix-free secondary ion mass spectrometry (SIMS).[1,2] The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure are sampled through an orifice with a diameter of 400 µm into the first vacuum chamber, transported into a quadrupole ion guide, and accelerated by 10kV after exiting the ion guide. The water droplets impact on a dry solid sample (no matrix used) deposited on a stainless steel substrate. The secondary ions formed by the impact are transported to a second quadrupole ion guide and mass-analyzed by an orthogonal time-of-flight mass spectrometer (TOF-MS). EDI was applied to peptides, synthetic polymers, and inorganic materials. It was found that EDI/SIMS has a high sensitivity without damaging the sample underneath and the film thickness desorbed by a single collisional event is to be less than a few monolayers. An instant conversion (in subpicoseconds) of kinetic energy of the impinging water droplet to the internal energies of molecules in the colliding selvedge takes place, i.e., sample molecules in the shock-wave excited selvedge suffer from the electronic excitation leading to the desorption/ionization. In the EDI mass spectra for PET, several fragment ions were observed but the XPS spectra did not change with prolonged cluster irradiation. This indicates that the surface of PET was etched with little surface damage. In the EDI mass spectra for tin and silicon, the major secondary ions observed were protonated oxide ions such as $H^+(SnO)_n$ and $H^+(SiO_2)_n$. This suggests that the oxidative chemical etching takes place in the selvedge of the colliding interface resulting in the atomic-level surface etching. Acknowledgement: This work was supported by the Japan Science and Technology Agency

[1] K. Hiraoka, D. Asakawa, S. Fujimaki, A. Takamizawa, K. Mori, Eur. Phys. J. D 38 (2006) 225.

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

2:40pm **AS-WeA4 Application of TOF-SIMS and LEIS for the Characterization of Ultra-Thin Films**, ***T. Grehl****, D. Rading, E. Niehuis,* ION-TOF GmbH, Germany*, R. ter Veen, H. Brongersma,* Calipso BV, The Netherlands*, M. Fartmann, B. Hagenhoff*, TASCON GmbH, Germany

The continuous scaling of semiconductor devices (film thickness, junction depth) to smaller dimensions increases the challenges for the established analytical methods. In addition, new and more complex materials are introduced into the devices. Secondary Ion Mass Spectrometry (SIMS) and more recently Time-of-Flight (TOF-) SIMS have become workhorses for the semiconductor industry. The depth distribution of implants as well as impurities is regularly monitored using Cs and O_2 sputter depth profiles. Meanwhile sputter energies as low as 200 eV are routinely used in order to achieve a high depth resolution. Even at these low sputter energies the transient effects prevent establishing a reliable depth scale and deriving quantitative information on the first few nm. In addition, concentrations exceed the dilute limit, thus further complicating the quantification process.In this situation, complementary techniques become increasingly important. One of the emerging techniques is Low Energy Ion Scattering (LEIS) using high sensitivity analyzers. It is extremely surface sensitive and provides quantitative information on the outermost atomic layer of a solid. Low energy (1 – 10 keV) noble gas ions (He, Ne, ...) are used as projectiles. The energy of the back-scattered ions from elastic collisions is characteristic for the masses of the target atoms and is measured using an electrostatic energy analyzer. Quantification is comparatively straightforward and bulk standards can be used to determine the sensitivity factors. In addition, information can be gained on the surface near depth distribution of elements (1 – 10 nm) by measuring the extra energy loss of ions scattered in deeper layers (non destructive, "static mode"). This can be combined with conventional sputter depth profiling using a separate beam of low energy noble gas ions ("dynamic mode").

In order to compare the performance of LEIS with TOF-SIMS results for the characterization of ultra-shallow layers we studied a variety of typical sample systems such as ultra-shallow As implants, high-k films, and diffusion barriers at different stages of ALD growth. The results are discussed with respect to information depth, ease of quantification and sensitivity. It can be shown that the static profiling approach of LEIS is extremely powerful in the first few nm of the profile whereas due to its higher sensitivity SIMS performs better after sputtering through the transient region.

3:00pm **AS-WeA5 Use of Ion-Solid Interaction Theory to Optimize FIB Processes**, ***L.A. Giannuzzi***, FEI Company

Focused ion beam (FIB) techniques have been used over the years to prepare specimens for characterization in a wide range of analytical instruments. One of the more popular uses of FIB is for the production of transmission electron microscopy (TEM) specimens. The advent of FIB for the preparation of specimens for 3D atom probe tomography (APT) allows for analysis of multi-phased and multi-layered materials which in the past would have been considered difficult or impossible due to specimen preparation constraints. In addition, FIB prepared surfaces are now routinely used for the acquisition of electron backscatter diffraction (EBSD) patterns. This technique has been extended to the acquisition of 3D crystallography in a DualBeam (FIB+SEM) instrument. Typical FIB instruments operating at 30 keV can result in sufficient lateral ion implantation and/or amorphization surface damage to hinder quantitative high resolution TEM results. Amorphization damage can also degrade the quality of the EBSD pattern such that the pattern cannot be resolved. In addition, 30 keV FIB milling can cause sufficient ion mixing which can destroy the chemical/elemental integrity of interfaces, rendering the 3D APT analysis useless. New advances in ion columns allow for imaging and FIB milling to take place down to 500 eV. Specimens can be prepared using the fine probe size of the high energy beam, and then polished with low energy ions which replace the high energy implantation damage with minimal damage from the lower energy ions. These low energy FIB techniques allow for quantitative high resolution (S)TEM, improve the quality of the EBSD patterns, and allow for 3D APT without interferences from the Ga+ ion implantation. In addition, since materials exhibit different collision cascade characteristics as a function of incidence angle, prototyping can be optimized by controlling the incidence angle and scan direction of the ion beam which can influence the profile and aspect ratio of the milled region.

4:00pm **AS-WeA8 C60 Bombardment of Si - New Insights from SIMS and TEM**, ***G. Gillen***, *C. Szakal, A. Herzing, I. Anderson,* National Institute of Standards and Technology, *S. Hues,* Micron Technology, *J. Bennett*, Process Characterization Laboratories, ATDF

There is continued interest in the development of novel cluster primary ion beams for applications in Secondary Ion Mass Spectrometry (SIMS). A C60 primary ion incident on a silicon substrate with an impact energy of 3000 eV would dissociate into 60 carbon atoms, each with an impact energy of only 50 eV. Since the depth resolution of a SIMS depth profile is directly related to the primary projectile energy, the use of such a cluster ion provides a possible method for obtaining ultra-high resolution SIMS depth profiles. Based on our previous experience with depth profiling of semiconductor materials using smaller cluster beams, it was hoped that C60 cluster SIMS would provide large improvements in depth resolution over conventional SIMS. Unexpectedly, initial evaluation of C60 SIMS depth profiling using delta-doped test samples demonstrated that deposition of an amorphous carbon layer on the silicon substrate was common, limiting the utility of C60 for depth profiling at impact energies below ~12 keV. Higher bombardment energies can minimize deposition but substantial degradation in depth resolution is observed compared to conventional SIMS depth profiling. This degradation was initially thought to result only from the formation of surface topography. In this work we have investigated the nature of the altered layer produced by C60 bombardment of silicon using SIMS and cross sectional transmission electron microscopy (TEM). Surprisingly, TEM imaging suggests the depth of penetration of carbon into the silicon substrate is substantially greater than would be predicted by simple ion implantation models. Furthermore, the buried interface between crystalline silicon and the carbon-rich altered layer exhibits nm scale roughness. These observations may help to explain the degradation in depth resolution commonly observed in C60 depth profiling of silicon materials. The enhanced diffusion of carbon beyond the penetration depth of the C60 may by explained by the enhanced diffusion of carbon in silicon resulting from strain produced in the silicon by high dose carbon implantation.

4:20pm **AS-WeA9 Understanding the Relationship between Chemical Vapor Deposition Precursor Structure and Film Properties by Application of Electron, Optical, Ion, and X-ray Characterization Methods**, ***B.W. Schmidt***, *B.R. Rogers, R.D. Geil*, Vanderbilt University

Ceramic oxides such as Al_2O_3 and HfO_2 are desirable in microelectronics as high-κ replacements of SiO_2 and in high temperature applications as protectants. For multi-component systems like CMOS devices and thermal barrier coatings, characterization and control of bulk and interfacial properties are important for optimal performance. Chemical vapor deposition (CVD) is popular for its high deposition rates and good conformality. However, final properties of a CVD film can be greatly influenced by the choice of precursor. Novel precursor ligand designs are used to increase volatility and precursor throughput, but can also affect film composition, microstructure, and the deposition window. In this study, ligand effects are investigated by understanding the deposition processes of dimethylaluminum isopropoxide (DMAI) and methylaluminum di-isopropoxide (MADI). These are derivatives of popular precursors trimethylaluminum (TMA) and aluminum tri-isopropoxide (AIP). TMA is well-suited for CVD bubbler delivery systems due to its high vapor pressure and liquid state at room temperature, but is dangerous to handle and requires an oxidant source. AIP has the advantage of being a single-source precursor for Al_2O_3, but requires melting at 130°C to achieve consistent precursor flux. DMAI and MADI represent one and two methyl-isopropoxide substitutions of TMA, respectively. A goal is to achieve a single precursor with beneficial characteristics of TMA and AIP. Film characterization by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), spectroscopic ellipsometry, and medium energy backscattering spectrometry provide insight into initial stage and bulk deposition. Correlation of composition, microstructure, and chemical state progression to deposition conditions will aid in the development of application-specific precursors.

4:40pm **AS-WeA10 The Interface Formation between Calcium and Poly(3-hexylthiophene) Investigated with Adsorption Microcalorimetry, High-Resolution XPS and ISS**, ***F. Bebensee***, Universitaet Erlangen, Germany, *J.F. Zhu,* University of Science and Technology of China, *J.H. Baricuatro, J.A. Farmer, W. Lew,* University of Washington, *H.-P. Steinrueck, J.M. Gottfried,* Universitaet Erlangen, Germany, *C.T. Campbell*, University of Washington

Regioregular poly(3-hexylthiophene) (rr-P3HT), a semiconducting polymer, is widely used in organic electronics (OLED, OFET). Both the interface structure and the interaction strength between the polymer and the electrode (e.g. Ca) are very important for the performance of such devices. The heat of adsorption, which directly reflects the bonding energy between the metal and the polymer, was probed using adsorption microcalorimetry. We find high initial heats of adsorption indicating a strong interaction between Ca and rr-P3HT. In high-resolution X-ray photoelectron spectroscopy (XPS) experiments, a substantial shift of the S 2p signal suggests electron transfer from Ca to S in the polymer. We therefore conclude that the high initial heat of adsorption is due to the interaction of Ca atoms with S in the sample. Furthermore, shifts of the C 1s signal imply a band bending of about 0.5 eV, while no hints for structural degradation of the polymer can be found. Ion scattering spectroscopy (ISS) measurements suggests that the initial Ca reacts below the surface, followed by 3D Ca island growth. Both of these observations are corroborated by the XPS measurements. We also investigated the effects of electron irradiation of the polymer surface prior to Ca evaporation. Financial support by the DAAD and the NSF is gratefully acknowledged.

5:00pm **AS-WeA11 Synthesis and Characterization of Core/Shell Nanoparticle Thin Films for Gas Analytical Microdevices**, ***M. Bruns***, *M. Fuchs, R. Ochs, S. Schlabach, D.V. Szabó,* Forschungszentrum Karlsruhe GmbH, Germany, *T. Grehl, S. Kayser,* ION-TOF GmbH, Germany, *M. Fartmann*, Tascon GmbH, Germany

Sputtered SnO_2 thin films are well established as gas sensing layers in analytical micro systems such as the Karlsruhe micro nose (KAMINA). To improve the performance towards higher sensitivity a very promising approach is to replace the sputtered thin films with films made of SnO_2 nanoparticles. This can easily be achieved by the Karlsruhe microwave plasma process (KMPP), a versatile precursor based gas-phase plasma process suited to synthesize nanoscaled particles with diameters less than 5 nm.[1] Regarding long-term stability, such SnO_2 nanoparticles can be coated in-situ with a protective ultra-thin SiO_2 shell in a downstream step and then directly deposited onto the respective micro devices. These core/shell nanoparticles are expected to prevent the gas sensitive core from growing and agglomeration, respectively, while preserving electrical contact. The prerequisite is to achieve an inhomogeneous SiO_2 shell enabling direct contact between adjacent SnO_2 nanoparticles, i.e. simply acting as a spacer.

This contribution focuses on the characterization of nanoparticle thin films with a thickness of 200 nm made of core/shell SnO_2/ SiO_2 nanoparticles by means of X-ray photoelectron spectroscopy (XPS). The main points of interest in this context are chemical binding states and information on the shell thickness in a non-destructive manner. For this purpose, the SiO_2 shell thickness systematically was increased while keeping the SnO_2 core size constant. In case of the desired inhomogeneous ultra-thin SiO_2 shells low energy ion scattering (LEIS) solely is a suitable means to distinguish between Sn and Si within the outermost monolayer of the spherical particles to prove the attainability of open-pored coatings. In addition, transmission electron microscopy (TEM), X-ray diffraction (XRD), and He-Pycnometry were used to achieve a comprehensive characterization.

[1] B. Schumacher, R Ochs, H. Troesse, S. Schlabach, M. Bruns, D. V. Szabó, J. Haußelt, Plasma Process. Polym. 4 (2007) 865.

5:20pm **AS-WeA12 Molecular Depth Profiling for Soft Materials by using Size-Selected Large Cluster Ions**, ***J. Matsuo***, *S. Ninomiya, H. Yamada, K. Ichiki, Y. Nakata, T. Aoki, T. Seki*, Kyoto University, Japan

Interest in soft materials, such as polymers or biological materials, has increased in the last decade. SIMS analysis and molecular depth profiling of soft materials with polyatomic and cluster ions have been demonstrated recently. The multiple collisions and high-density energy deposition of these ions on solid surfaces induce enhancement of sputtering and secondary ion yields, as well reduced residual surface damage compared with other techniques. We have demonstrated that the sputtering yields of polymer and amino acids with large Ar cluster ions (mean size: 1000) at the energy of 20 keV are more than 100 molecules/ion, and sputtered surfaces are much smoother than the original surfaces. Secondary ions emitted from arginine (Arg, C6H14N4O2), leucine (Leu, C6H13NO2), glycylglycylglycine (GlyGlyGly, C6H11N3O4), polymethyl methacrylate (PMMA), and tris (8-hydroxyquinoline) aluminum (Alq3, C27H18AlN3O3) films were measured using the time-of-flight (TOF) technique under the incidence of large Ar cluster ions at incident energies of 3 and 20 keV. The ratio of fragment ions to molecular ions decreases quite rapidly with increasing cluster size. Very few fragment ions were observed in the mass spectrum, when the cluster size was larger than 1000. The kinetic energy of a few eV/atom is comparable to the bonding energy of molecules. We have found that residual damage is strongly dependent on the incident velocity of cluster ions, when the size of the cluster ion is larger than 100, and this result is well matched with recent MD simulations. Ultra-low energy SIMS and molecular depth profiling of various soft materials can be realized by using large Ar cluster ions. Recently, molecular depth profiling with low energy (<500eV) monomer ions has also been reported for various polymers. However, in order to realize molecular depth profiling the primary monomer ion beam has to be carefully chosen. The atomistic mechanism of energetic large cluster impacts and the prospects of this technique will be discussed in conjunction with the size effect in secondary ion emission and damage cross-section.

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

Advances in Surface Analytical Methods for Organic and Biological Interfaces
Moderator: D.W. Grainger, University of Utah

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

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

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

Understanding the chemistry of barnacle adhesion is of great interest in the areas of marine biofouling prevention and materials science of adhesives. While most work on the chemistry of barnacle adhesion to date has focused on identifying the protein composition of barnacle cement, relatively little has been done to directly characterize structure of barnacle cement proteins in their native states. Such studies should provide further insight into relationships between chemical structure and adhesion, as well as the types of biochemical mechanisms that may play roles in barnacle cement curing. We have used atomic force microscopy (AFM), circular dichroism (CD), and Fourier transform infrared (FTIR) spectroscopy to characterize cements deposited on quartz and CaF_2 substrates in seawater by barnacles (Amphibalanus amphitrite) transferred from silicone release panels. AFM imaging consistently shows that secondary cement residues left on the substrates are fibrillar. Circular dichroism spectra of cement residues on quartz showed negative peaks centered near 225 nm and positive peaks at about 195 nm, indicating that the barnacle cements are primarily helical in structure, but also contain some β-sheet components. This is further confirmed by transmission FTIR of cement residues on CaF_2, for which the amide III band is found to be composed of a broad band centered ~ 1650 cm^{-1} consistent with α-helical structures, and components near 1685 and 1630 cm^{-1} consistent with β-sheet structures. These results suggest that the fibrillar structures are predominantly helical in structure, in contrast with fibrillar structures like amyloids that exhibit primarily β-sheet conformations.

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

Secondary ion mass spectrometry (SIMS) is based on the acceleration of primary ions onto a target. Secondary electrons, neutrals and ions are emitted from the target reflecting its chemical composition. SIMS is unique in its ability to detect simultaneously several target molecules in compound samples and to image their localization at subcellular resolution. The aim of the project is to develop the technology of imaging TOF-SIMS as a tool in biomedical research for analysis and localization of relevant target molecules e.g. inorganic ions, lipids, drugs, carbohydrates and proteins in the same sample. Recent research in TOF-SIMS has shown the distribution of a wide variety of compounds in biological tissue. The current issues in TOF-SIMS analysis are the data interpretation and identification of all new peaks detected with this technique. Until 2004, only a few high mass peaks of biological origin were identified, which leaves us in a situation where much of the interpretation of spectra remains to be done. The aim of this presentation is to define analyte molecules by mass spectra obtained using new primary ion sources with unique fragmentation properties. The possibility to detect proteins is of special interest. It is also an aim of the project to educate students in the analysis of cells and tissue with a high technology method as the research group is presently purchasing our own TOF-SIMS instrument.

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

Creating images with mass spectrometry (MS) at <10 micron scale resolution is a substantial challenge due to diffusion effects and low signal levels. A new instrument is described for laser desorption and in-source postionization (LDPI) imaging mass spectrometry with enhanced performance over the previous non-imaging instrument.[1] A significant fraction of the desorbed molecules are intercepted by a vacuum ultraviolet (VUV) postionizing laser, then extracted into the time-of-flight (TOF) mass analyzer. Postionization provides a higher and more consistent sensitivity than matrix-assisted laser desorption/ionization for certain analytes, thereby enhancing imaging MS on this small length scale. The instrument utilizes 349 nm laser desorption with 5 micron minimum spot size, 157 nm laser postionization and will operate at ~200 Hz. Samples are analyzed in microprobe mode and are imaged by rastering the x-y stage. The ion source also incorporates digital optical imaging of the sample surface, which allows for correlation of MS and optical images. The orthogonal geometry of the ion source provides for good separation of direct ion signal and postionized signal by varying the extraction delay, leading to enhanced mass resolution. Use of LDPI-MS is demonstrated for the detection of antibiotics within intact bacterial biofilms.[2] Staphylococcus epidermidis is a common Gram positive bacterium that resides on human skin and is one of the most frequent culprits behind hospital acquired biofilm infections. Treatment of biofilm infections is hindered by the limited ability of antibiotics to kill biofilm associated microbes. LDPI-MS is used to detect antibiotics within intact biofilms without significant interference from other biofilm chemical constituents. Sulfadiazine is detected these biofilms at relatively high concentrations while tetracylcine is detected at near clinical concentrations. These results indicate that imaging MS of bacterial biofilms, animal tissue, or other biological samples by LDPI-MS can be applied to analysis of low ionization potential analytes such as the described antibiotics and other compounds including pharmaceuticals.

[1] M. Zhou, C. Wu, A. Akhmetov, P.D. Edirisinghe, J.L. Drummond and L. Hanley, J. Amer. Soc. Mass Spectrom. 18, 1097 (2007).

[2] G.L. Gasper, R. Carlson, A. Akhmetov, J.F. Moore and L. Hanley, Proteom. (2008) in press.

4:00pm **BO+AS+BI-WeA8 3D Mass Spectrometric Analysis of Non-Dehydrated Biological Samples**, ***H.F. Arlinghaus***, *J. Möller, C. Kriegeskotte, D. Lipinsky*, Westfälische Wilhelms-Universität Münster, Germany

ToF-SIMS and laser-SNMS are increasingly important tools for analyzing the elemental and molecular distribution in biological samples. However, in-vivo analyses of tissues or cell cultures are impossible because the sample must accommodate the vacuum conditions of the instrument. Thus, fixing the sample in its vital state, such as freezing, is essential. Sample preparation by cryo-fractioning or cryosectioning techniques followed by freeze-drying has been successfully used. However, these techniques exhibit several limitations. In order to overcome these limitations, a combination of a ToF-SIMS/laser-SNMS instrument and an in-vacuum cryosectioning instrument were developed for directly preparing and analyzing frozen non-dehydrated samples. The correct sample temperature after preparation and during the analysis showed to be a major factor for the quality of suitable ToF-SIMS/Laser-SNMS analyses. On the one hand, it is necessary to keep the sample cold to avoid freeze drying, on the other hand, a slight increase of the sample temperature removes adsorbates formed by residual gas in the cutting chamber and, more importantly, water resulting from the cutting process, and anticipates adsorption during the analysis. In our presentation, we will show and discuss how to optimize the sample's temperature, sample preparation techniques for analyzing various biological samples, and the possibility of obtaining 3D molecular images of frozen non-dehydrated biological samples. Our data will show that both TOF-SIMS and Laser-SNMS are capable of imaging elements and molecules in complex biological samples and that they are very valuable tools in advancing applications in life sciences.

4:20pm **BO+AS+BI-WeA9 Construction of Complex Two- and Three-Dimensional Nanostructures: Combined Time-of-Flight Secondary Ion Mass Spectrometry and Microscopy Studies**, *C. Zhou, P. Lu, **A.V. Walker***, Washington University in St. Louis

Methods for the chemically selective deposition of metals, semiconductors, biomolecules and other compounds have been studied and applied to the construction of complex multilayer structures. This work has important applications in molecular and organic electronics, sensing, biotechnology and photonics. To illustrate our approach we present two examples: the chemical bath deposition (CBD) of zinc sulfide on functionalized SAMs and the construction of three-dimensional nanostructures via layer-by-layer growth. CBD is a solution-based method for the controlled deposition of semiconductors. ZnS is a direct band-gap semiconductor used electroluminescent devices and solar cells. Two sizes of crystallites are observed to form: ~500 nm nanoflowers and ~2 µm crystallites. Nanoflowers nucleate at Zn(II)-carboxylate terminal group complexes on -COOH terminated SAMs. They grow via an ion-by-ion reaction pathway and remain chemically bound to the SAM. In contrast, the micron-sized crystallites form in solution (cluster-by-cluster growth) and are observed on all SAMs studied (-OH, -COOH and -CH_3 terminated SAMs). These crystallites can be easily removed from the surface using sonication. Thus under the appropriate experimental conditions ZnS can be selectively deposited onto -COOH terminated SAMs. We illustrate this by selectively depositing ZnS on a patterned -COOH/-CH_3 terminated SAM surface. Our approach for the construction of three-dimensional nanostructures begins with a single SAM layer deposited and UV-photopatterned using standard techniques. A second layer is then assembled by specific chemical reaction with the terminal groups of the first SAM. Additional layers are deposited using the same method. Experiments to date have focused on the specific coupling reaction of amines with carboxylic acids to form multilayer structures. Using TOF SIMS imaging we have followed each step of this reaction and have been able to demonstrate the selective formation of multilayer structures on patterned -COOH/-CH_3 surfaces. This coupling is used to make several proof-of-concept multifunctional structures.

4:40pm **BO+AS+BI-WeA10 TOF-SIMS Analysis of Lipid Transfer between Vesicles and Supported Lipid Bilayers on TiO_2**, ***P. Sjovall***, SP Technical Research Institute of Sweden, *A. Kunze, B. Kasemo, S. Svedhem*, Chalmers University of Technology, Sweden

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) was used to investigate the electrostatically driven lipid transfer between negatively charged vesicles (POPS) and a positively charged supported lipid bilayer (POEPC) on a TiO_2 surface. Quartz crystal microbalance with dissipation (QCM-D) was used to monitor the formation of the POEPC bilayer (by vesicle adsorption and rupture), the subsequent interaction with POPS vesicles, and the resulting lipid transfer between the bilayer and the vesicles. In addition, QCM-D showed that SDS treatment of the bilayer after lipid transfer removed mass corresponding to one of the lipid leaflets (seemingly leaving a lipid monolayer), and that a bilayer could be reformed upon POEPC vesicle adsorption on this monolayer. TOF-SIMS analysis using Bi_3^+ primary ions was used to provide quantitative estimates of the lipid composition in the different lipid layers. The lipid bilayers were prepared for TOF-SIMS analysis by plunge freezing and freeze drying(1). In order to allow for unambiguous detection of POPS in the lipid bilayers, POPS with fully deuterated palmitate fatty acid tail groups was used in the buffer vesicles. Quantitative estimates of the lipid compositions were made based on the signal intensities from the deuterated (POPS) and undeuterated (POEPC) palmitate ions, as well as from the oleate (POPS and POEPC) ion, using a simple model for the concentration-dependent TOF-SIMS signal intensities. Reference bilayers prepared with known lipid compositions were analysed in order to provide calibration points for the quantitative analysis. The results show that the POEPC bilayer after lipid transfer contains approximately 50% POPS, while the SDS-resistant monolayer contains about 70% POPS and the reformed bilayer contains 20-25% POPS. Possible asymmetries in the lipid composition of the bilayers were, however, not taken into account. A number of peaks, which can be assigned to molecular ions of POPS, were observed in the negative ion spectra of the POPS-containing lipid bilayers. Interestingly, these peaks were absent in the spectra from the SDS-resistant monolayer, although the signal from the deuterated palmitate ion indicated about 70% POPS in the monolayer. This suggests that the POPS molecular peak only shows appreciable intensity in TOF-SIMS spectra from the bilayer structure, similar to what has been observed previously for POPC.[1]

[1] Prinz et al., Langmuir 2007, 23, 8035-8041.

5:00pm **BO+AS+BI-WeA11 Spatial Distribution Analysis of a Selenium Based Anti-Cancer Drug in Tumor Tissue Samples by ToF-SIMS**, ***S.A. Burns***, University at Buffalo, *M. Khin, L. Kazim, Y. Rustum, S. Cao, F. Durrani*, Roswell Park Cancer Institute, *J.A. Gardella*, University at Buffalo

Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) has recently found new applications in the field of tissue analysis due to the advancement of cluster ion sources.[1] Bi cluster primary ion sources have been shown to produce chemical images with high spatial resolution, to ca. 100nm. The use of C60 cluster ion sources for depth profile analysis distributes the ion impact force allowing for a more specialized analysis of organic samples.[2] ToF-SIMS is an extremely useful application to detect low molecular weight drugs within a polymeric membrane. This study utilized this application to spatially image drug distribution of an anticancer agent in a two types of tissue samples. Nude mice implanted with human head and neck tumors were treated with methylselenocystein (MSC), a known anticarcinogen.[3] MALDI imaging has been used to determine the distribution of another anti-cancer drug, CPT-11 when MSC has also been introduced.[4] The distribution of CPT-11 was found to be more even throughout the tumor in the presence of MSC. This indicates that the MSC causes an increase the vasculature of a tumor thereby allowing other anti-cancer drugs to distribute evenly. MALDI imaging was able to show drug distribution but could not associate the fragment peak of the MSC with the vasculature of the cells due to restrictions in image resolution (100µm). ToF-SIMS imaging has been shown to reach resolutions of 100nm allowing for this type of analysis to be performed. MSC treated tumor and liver samples were analyzed using imaging and depth profiling to determine the distribution of drug with respect to the vasculature of the tissue. The first step of this study was to determine characteristic peaks from the MSC that could be identified in the tissue samples. Analysis of the livers and tumors of the mice that had been treated with MSC had fragment peaks with isotopic distributions indicating selenium containing organic compounds not found in the control samples. These fragment peaks were used as the drug peaks whose distribution in the tissue samples were compared to fragment peaks which could be attributed directly to cell vascular structure.

[1] Brunelle,A,et al. Journal of Mass Spectrometry 2005,40,985-999

[2] Fletcher,JS,et al. Analytical Chemistry 2006,78,1827-31

[3] Azrak,RG,et al. Biochemical Pharmacology 2007,73,1280-1287

[4] Prieto Conaway,MC,et al. Thermo Scientific 2008,Application Note.

5:20pm **BO+AS+BI-WeA12 Effects of Different Sample Preparation Methods for Cell Imaging using TOF-SIMS**, ***J. Malm***, SP Technical Research Institute of Sweden, *D. Giannaras*, University of Glasgow, UK, *P. Sjövall*, SP Technical Research Institute of Sweden, *N. Gadegaard, M.O. Riehle*, University of Glasgow, UK

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is increasingly being used for chemical imaging of cells and tissue. A concern in these studies is that the samples need to be prepared for the vacuum environment. Several sample preparation methods exist for this purpose. In this work, effects of different preparation methods on the structure and surface chemistry of human fibroblast hTert cells were studied. Two fixation protocols, using glutaraldehyde (GA, $C_5H_8O_2$), and osmium tetroxide (OsO_4), respectively, were compared to a non-fixing protocol where cells were washed with ammonium formate (AF, NH_4HCOO) prior to drying. Three drying techniques were compared, namely freeze-drying (FD) after rapid plunge-freezing, critical point-drying (CPD), and alcohol ladder-drying (ALD). Imaging TOF-SIMS with Bi_3 cluster primary ions was used to compare the different preparation protocols with respect to surface chemistry, and the structure of the cells after preparation was studied using scanning electron microscopy (SEM). For the AF-washed samples, changes in cell volume was followed by interference reflection microscopy (IRM). The results show that both the fixation/washing protocols as well as the drying protocols affect the chemical information obtained in TOF-SIMS analyses. For GA-fixed samples, both CPD and ALD give rise to reduced phosphocholine (PC) signal on the cell surface by two orders of magnitude, as compared to FD, while no significant differences are seen for cholesterol and amino acid fragment ions. GA-fixed samples post-fixed using OsO_4 showed PC intensities reduced by only one order of magnitude, going from FD to CPD or ALD. The cholesterol intensity was found to be higher for AF-washed cells and cells fixed with OsO_4, than for GA fixed cells. An increase in amino acid intensity going from AF to GA to OsO_4 was also observed.

Nanomanufacturing Focus Topic
Room: 309 - Session NM+PS+AS-WeA

Nanomanufacturing I: Plasma Processing and Materials
Moderator: R.M. Martin, IBM T.J. Watson Research Center

1:40pm **NM+PS+AS-WeA1 Silicon Nanocrystal Inks: Plasma Processing as a Route to Solution-Processed Silicon Films**, ***U.R. Kortshagen***, *R. Cram, D. Rowe, X.-D. Pi*, University of Minnesota **INVITED**

Colloidal nanocrystals are studied for a wide spectrum of applications from more efficient quantum dot solar cells to printed electronics. While significant advances have been made with chalcogenide semiconductors, similar progress with silicon has been hampered for a long time by the lack of efficient synthesis approaches. However, silicon has the undoubted advantage of being non-toxic, environmentally benign, abundant and cheap. This talk describes a plasma synthesis approach for the efficient synthesis of silicon nanocrystals. Silicon crystals are synthesized in a flow through plasma reactor on time-scales of a few ms. The residence time of the silicon crystals can be used to tailor the nanocrystal size. Dopants can be introduced into the crystals and changes in the photoluminescence properties as well as surface etching studies allow to deduce the dopant location within the nanocrystal. The nanocrystal surfaces can be functionalized with organic ligands that impart solubility to the nanocrystals. By making silicon nanocrystals soluble in organic solvents, inks of doped silicon crystals can be formed that can be used to prepare silicon nanocrystal films through solution processes such as drop coating, spin coating, or ink-jet printing. Laser annealing is used to produce conducting films from the colloidal nanocrystal precursors. Structural and electrical properties of the films are determined with a wide array of characterization techniques. Properties and potential applications of these materials will be discussed.[1]

[1] This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-0212302. Partial support is acknowledged by NSF grant DMI-0556163, and by Center for Nanostructure Applications at the University of Minnesota.

2:20pm **NM+PS+AS-WeA3 Vertically Aligned Si Nanostructure Arrays formed using SF$_6$/O$_2$ Plasma**, ***C. Yang***, *S.H. Ryu, Y.D. Lim, W.J. Yoo*, Sungkyunkwan University, Korea

Arrays of high aspect ratio (>10:1) vertically aligned Si nanostructure were formed in an inductively coupled plasma (ICP) reactor using SF6/O2 plasma without any masks at noncryogenic temperature. Mean diameter of the nanostructure arrays is about 100 nm and the mean height is up to 4.77 um. These nanostructure arrays can be fabricated for large area (>100 cm2). The formation of the nanostructure arrays are studied as a function of time, bias RF-power and O2/SF6 ratio. The processing condition of the SF6/O2 plasma is known to markedly affect the preparation of the nanostructure arrays. O2/SF6 ratio determines the formation of the nanostructure arrays. The nanostructure arrays only could be fabricated when the O2 content is not too low or too high, the range is 0.5< O2/SF6<2.5. Two types of the nanostructure arrays formed because of the different bias RF-power, one is nanohole arrays and another is the nanopillar arrays. The formation of the nanostructure is hole when the bias power is 10 W, but the diameter is only 420 nm after etching 150 s. If the bias power increased to 30 W, the nanopillar arrays appear, the mean height is up to 4.77 um after etching 150s. The etching time is also important for the nanostructure arrays. After etching about 40s, the nanostructure arrays appear abruptly and become longer and longer. But very long time etching has destroyed the nanostructure arrays. The mechanism of the plasma etching for fabricating the nanostructure arrays has been investigated using OES, XPS and SEM analyses. From the analyses, the properties of the plasma and the formed passivation layer are mainly reasons for the fabrication of the nanostructure arrays. The best condition to fabricate a high aspect ratio vertically aligned Si nanostructure arrays is suggested.

2:40pm **NM+PS+AS-WeA4 Structured Growth of Silver Nanoparticles Within a Hydrocarbon Matrix**, ***E. Körner***, *J.F. Lübben, G. Fortunato, D. Hegemann*, EMPA, Switzerland

Low pressure plasma processes enable an extensive variety of surface adjustments for medical applications or technical textiles. Specifically, a modular plasma vacuum chamber provides the base for highly flexible and tailor-made coating technology. Different modification strategies, e.g. activation, etching, plasma polymerization or metallization by sputtering can be used separately or combined with each other. This work presents the combination of plasma polymerization and etching with a co-sputtering process which leads to the formation of a nanoporous polymer matrix with embedded metal nanoparticles. A capacitively coupled radiofrequency power input and an asymmetric reactor geometry allow the production of such multifunctional coatings within in a one-step process. The hydrocarbon matrix is built-up by using ethylene (C_2H_4) as a monomer gas. In addition, carbon dioxide (CO_2) or ammonia (NH_3) is used as the reactive gas, to structure the matrix and add functional groups to the a-C:H network. The deposition rate and the functionality of the coatings are adjusted by the ratio of reactive gas to monomer. With increasing the ratio of reactive gas the functionality of the matrix increases at the expense of the deposition rate. An excess of argon is used in the gas mixture for co-sputtering from a Ag cathode. The growth, distribution and formation of Ag particles are analyzed carefully under different conditions with respect to the gas mixture. The films are investigated with atomic force microscopy and scanning electron microscopy after different growth steps. It can be seen that the particles are more embedded in the matrix for higher film thicknesses and lower reactive gas ratios. Additionally, X-ray photoelectron spectroscopy analyses are performed to evaluate the surface chemistry and Ag surface concentration. For bulk measurements, the overall Ag content is measured with inductively coupled plasma optical emission spectrometry. Target covering or oxidation can decrease the Ag deposition rate and has to be taken into account in determining the optimal plasma conditions. In contrast to magnetron sputtering the Ag particles appear to be bigger with RF sputtering, which could provide a Ag reservoir with a slower release and a better long-term antibacterial effect. This is important for the application of the films as antibacterial coatings, where an optimal antibacterial efficiency for a minimal amount of Ag is desirable.

3:00pm **NM+PS+AS-WeA5 Photoluminescence Brightening from Freestanding Single-Walled Carbon Nanotube Bundles Prepared by Diffusion Plasma CVD**, ***R. Hatakeyama***, *T. Kato*, Tohoku University, Japan

The optical property of single-walled carbon nanotubes (SWNTs) has been the subject of intense interest in recent years, since the discovery of efficient photoluminescence (PL) from isolated semiconducting SWNTs. Because it was believed that the debundle of SWNTs was the inevitable process to capture the PL signal from SWNTs, the bundle forming SWNTs were, in most cases, treated as by-products or impurities causing a spectrum broadening and shifting, and hence their optical features, especially the PL, have not attracted a great deal of attentions so far. Very recently, the PL from bundled SWNTs in an aqueous solution has been reported. Since the PL from bundled SWNTs includes outstanding advantages such as an exemption from a complicated debundle process and easy manipulation, it can be expected that the SWNT-bundle engineering has a great potential for the nanotube-based PL device fabrication. From an industrial point of view, the application of nanotube-PL to the well-organized present semiconductor technology is an inevitable factor, i.e., the establishment of bright PL emission from a solid-state material is considered to be a still remainded fundamental problem. In this study we report unique PL features obtained from as-grown vertically-, and individually-freestanding SWNTs prepared by a diffusion-plasma chemical vapor deposition method.[1] The intensity of PL is clearly observed to increase through the morphology transition from isolated to thin-bundled of the freestanding SWNTs.[2] Based on the precise spectrum analysis and equation-based estimation of the PL time trace, the origin of the PL brightening is consistently explained in terms of the exciton energy transfer through the tube bundles. The PL brightening is also revealed to obviously depend on SWNT diameters. Only the small-diameter rich sample can realize the PL brightening, which can be interpreted to be due to the different concentration of metallic SWNTs causing a PL quenching. Since it appears to be possible to fabricate brightly illuminating nanotubes on various kinds of substrates, the bundle engineering with freestanding nanotubes is expected to be a potential candidate for realizing the nanotube-based PL device fabrication.

[1] T. Kato and R. Hatakeyama, Appl. Phys. Lett., 92 (2008) 031502.

[2] T. Kato and R. Hatakeyama, J. Am. Chem. Soc., accepted.

4:00pm **NM+PS+AS-WeA8 Practical Considerations for Implementation of Nanomaterials in Aerospace**, ***K.D. Humfeld***, The Boeing Company **INVITED**

4:40pm **NM+PS+AS-WeA10 Large-Scale Production and Metrology of Vertically Aligned Carbon Nanotube Films**, ***L. Dai***, *K. Bosnick*, National Research Council Canada

We have successfully produced carbon nanotube (CNT) films (25-50 wafers per load) on a large scale in a commercial Tystar chemical vapor deposition (LPCVD) system. Electron microscopy studies indicate that the CNT films are consisted of densely packed and vertically aligned multi-walled CNTs. A series of catalysts and growth conditions are tested systematically to synthesize high quality CNTs by varying the catalytic metal compounds and the CVD parameters. Both Fe films and ternary metal Cr/Ni/Fe films have been found favorable for the growth of aligned CNT films. To assess the as-grown vertically aligned CNT films, we are developing a general metrology which contains various analytical techniques to qualify the CNT film morphology, size, chirality, homogeneity, purity, dispersion, etc. This metrology uses some of the measurement equipments that are broadly used for material characterizations, including scanning electronic microscopy (SEM), transmission electron microscopy (TEM), Raman spectroscopy, profilometry, contact angle measurement and thermo gravimetric analysis (TGA). The metrology will facilitate quality control and process optimization necessary for industry applications of CNT films.

5:00pm **NM+PS+AS-WeA11 Linewidth Measurements on sub-20 nm HSQ/Graphene Nanostructures**, ***J.J. Peterson,*** Intel Corporation*, M.A. Rodriguez, V. Tileli,* University at Albany-SUNY*, M. Sprinkle, C. Berger, W.A. de Heer*, Georgia Institute of Technology

Although linewidth measurements of patterned graphene nanoribbons using the high resolution (HR) scanning electron microscope (SEM) have been reported in the literature,[1] it is known that such measurments are generally destructive to the structures which are being measured. Furthermore, due to the destructiveness of the measurement, the critical dimensions may be changing even as the measurement is being made. For this reason, the atomic force microsope (AFM) and scanning probe microscope (SPM)[2] has become an accepted method of linewidth measurement for graphene or hydrogen silsesquioxane (HSQ) on graphene structures, but this methodology is not scaleable to a manufacturing environment. For this reason, it is desired that a more manufacturable method of linewidth measurement may be developed for measurement of critical dimensions of graphene nanostructures. In this talk, we compare linewidth measurements sub-20 nm HSQ/graphene structures using the HR SEM and environmental-SEM (E-SEM) and report that E-SEM measurements will support the necessary resolution to enable linewidth measurements of graphene nanostructures without the damage associated with typical HR scanning electron microscopes. Furthermore, we make a comparison of linewidth measurements using both the SPM and E-SEM and discuss each respective method's advantages and disadvantages.

5:20pm **NM+PS+AS-WeA12 Size Distributions and Agglomeration Effects in FePtAu Nanoparticles**, ***V.V. Krishnamurthy,*** Oak Ridge National Laboratory*, Z. Jia, D. Reed, M. Mandal, G.J. Mankey, J.W. Harrell, D.E. Nikles,* The University of Alabama*, L. Porcar*, NIST Center for Neutron Research

We have investigated the effect of thermal treatment on the microstructure and positional ordering of chemically synthesized $(Fe_{49}Pt_{51})_{88}Au_{12}$ nanoparticles using small angle neutron scattering (SANS). The as made FePtAu particles have an average diameter of 3 nm. Thin films of nanoparticles were prepared by spincoating the dispersion of FePtAu nanoparticle on Si wafers. The samples were annealed for 30 minutes in a flowing nitrogen atmosphere in order to promote FCC-L1_0 phase transformation. The annealing temperature of the samples was varied from 300 °C to 550 °C in steps of 50 °C. The crystal structure and the lattice constant of the samples have been determined by x-ray diffraction. The magnetization hysteresis has been measured in a vibrating sample magnetometer. SANS measurements were performed at room temperature with an incident neutron wavelength of 6 Å using the 30 m NG3 SANS instrument at NIST. The scattering vector magnitude (q) dependence of the SANS intensity, I(q) shows strong dependence on the sample annealing temperature. The q dependence of the SANS intensity in the range of 0.2 to 3 nm^{-1} could be fitted by modeling the nanoparticles as polydisperse spheres with Schultz distribution for the diameters and a hard sphere interaction between the particles. In this q range, the agglomerates are assumed to be polydisperse spheres. The results indicate that significant agglomeration occurs in all the samples. The average size of the agglomerates is found to increase from 18 nm at 300 °C to 53 nm at 550 °C. The data also seem to indicate the sintering of particles in the temperature range of 500-550 °C. These results will be compared with the particle size distributions in off-situ annealed $Fe_{49}Pt_{51}$ nanoparticles and in-situ annealed $(Fe_{49}Pt_{51})_{88}Au_{12}$ nanoparticles.

Thursday Morning, October 23, 2008

Energy Science and Technology Focus Topic
Room: 203 - Session EN+EM+NS+P+A+T+V-ThM

Energy: Tools and Approaches
Moderator: S.P. Williams, Plextronics, Inc.

8:00am **EN+EM+NS+P+A+T+V-ThM1 Nano-Structured and Micro-Structured Semiconductors for Better Efficiency of Solar Cells**, ***C.-F. Lin***, *J.-S. Huang, S.-C. Shiu, J.-J. Chao, C.-Y. Hsiao, K.-H. Tsai*, National Taiwan University **INVITED**

The foreseeable depletion of fossil fuel and the global warming caused by the carbon dioxide had led to the increasing attention of alternative renewable energy, especially photovoltaic. Therefore, crystalline Si-PV devices are quickly spreading. Unfortunately, the large consumption of Si materials hinders their vast applications. Many efforts have been switched to developing thin-film PV devices. In this talk, we will discuss the use of nano-structured and micro-structured semiconductors that enable the fabrication of thin-film solar cells with improved efficiency. Several types of such thin-film solar cells will be discussed, including the organic-semiconductor-nanowire composite film, organic-semiconductor micro-structure composite film, nano-wire semiconductor thin film, and micro-structured semiconductor thin film. In the thin-film solar cells using organic-semiconductor-nanorod composite film, different types of semiconductor nanowires such as ZnO, Si, and GaAs nanowires are used to replace the accepter-type organics for two purposes: increasing the electron mobility and assisting the formation of nano-morphology for better inter link between the donor organics and acceptor materials. The fabrication procedures of those nanowires as well as the formation of the organic-semiconductor-nanowire composite film with controlled nano-morphology will be presented. For the other solar cells using nano-structured and micro-structured semiconductors, we will particularly describe the technique of nanowire/micro-structure transfer. In our approach, the nanowires and micro-structures are made from the bulk semiconductors or epitaxial semiconductors, so they will have much better crystal quality than the usual thin-film materials. In addition, after nanowires and micro-structures are transferred to other transparent substrates, the original wafer can be reused, so the material cost can be lowered considerably. In addition, it offers the advantages of the bending flexibility, not being limited by the brittle property of semiconductors. Furthermore, in comparison with current III-V tandem solar cells taken by monolithic approach, which requires lattice match and current balance, our approach enables mechanically stacking. Thus each cell could be designed individually to match the entire solar spectrum for optimal solar usage. Therefore, such new-type thin-film solar cells are expected to be potentially efficient and low cost.

8:40am **EN+EM+NS+P+A+T+V-ThM3 Endohedral Metallofullerenes as Improved Acceptor Materials for Organic Solar Cells**, *M. Drees,* Luna Innovations Incorporated*, R. Ross,* Georgetown University*, C. Cardona,* Luna Innovations Incorporated*, E. Van Keuren,* Georgetown University*, D. Guldi,* Friedrich-Alexander-Universitat Erlangen-Nurnberg, Germany*,* ***B.C. Holloway***, Luna Innovations Incorporated

Cost factors in inorganic solar cells have opened up a new path to less expensive manufacturing techniques using bulk heterojunction polymer/fullerene based solar cells. Using empty cage fullerene derivatives as the acceptor material, state-of-the-art organic photovoltaics currently display ~5% overall conversion efficiency. One of the main factors limiting the efficiency in organic solar cells is the low open circuit voltage. The open circuit voltage is governed by the molecular orbitals of the donor and acceptor material; therefore better matching of the orbitals will lead to improved voltages. Here we present a novel acceptor material based on Trimetasphere® carbon nanomaterials (TMS). Trimetaspheres® are endohedral metallofullerenes that consist of a trimetal nitride cluster enclosed in a C80 cage. First-generation Trimetasphere® carbon nanomaterial derivatives have been synthesized and show behavior consistent with C60 but with improved molecular orbitals. Electrochemical data suggests a maximum voltage increase of up to 280 mV over C60-PCBM-based devices and photophysical characterization of shows efficient and stable charge separation. Initial bulk-heterojunction devices have been synthesized with open circuit voltages that are 280 mV higher than reference devices using C60-PCBM and conversion efficiencies exceeding 3.1%.

9:00am **EN+EM+NS+P+A+T+V-ThM4 Morphology Study of Vacuum-Deposited Pentacene:C60 Mixed Thin Films for Photovoltaic Applications**, ***J. Xue****, Y. Zheng, J.D. Myers, J. Ouyang*, University of Florida

The efficiency of organic photovoltaic (PV) devices has gained steady increase in past 20 years, showing a potential to provide clean and low-cost electrical energy in the near future. Bulk heterojunction (HJ) composed of nanoscale percolation of donor and acceptor phase have been demonstrated to improve the efficiency of organic PV device. Such improvement is attributed to the creation of a spatially distributed interface, which enhances exciton dissociation, and the presence of continuous conducting paths for efficient charge collection. However, ideal nanoscale percolation is not readily achievable. Therefore, understanding the morphology inside the bulk heterojuncion plays an important role on achieving efficient PV device. Here, phase separation in donor-acceptor (D-A) mixture composed of pentacene:C60 and how it contributes to a percolated morphology are studied. The pentacene:C60 mixed films are fabricated by co-deposition of two molecules with vacuum thermal evaporation (VTE) method. The mixing ratio of pentacene and C60 is controlled by varying the deposition rate of each species. X-ray diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM) are used to characterize the vacuum deposited pentacene:C60 mixed film. XRD patterns of pentacene:C60 mixed films indicate phase separation inside the mixture, which is reflected by appearance of characteristic diffraction peaks of thin film phase pentacene. SEM and AFM images reveal the change of surface morphology of the mixed films with varied mixing ratio and deposition rate, suggesting different degree of phase separation inside. Base on these information, PV devices are fabricated and their performance is investigated. It is found that by suppressing the phase separation between pentacene and C60 to nanoscale the PV performance is improved significantly. The open circuit voltage (Voc) and short circuit current (Jsc) increase from 0.45 V and 9.7 µA/cm2 in pentacene:C60 = 1:1 (by weight) device to 0.58 V and 1.3 mA/cm2 in pentacene:C60 = 1:5.5. All these suggest that degree of phase separation of molecular mixtures can be controlled by varying the process conditions, which may lead to new pathways to generate nanoscale percolation for application in efficient organic PV devices.

9:20am **EN+EM+NS+P+A+T+V-ThM5 Tailoring the Morphology of Organic Solar Cells with Surface Templates**, ***S. O'Donnell****,* University of Virginia and The MITRE Corporation*, P. Reinke*, University of Virginia

One of the most important applications of fullerenes is their incorporation in organic solar cells, where they function as an electron acceptor in conjunction with photoactive molecules such as porphyrin. The photoyield is intimately linked to the morphology, which determines the efficiency of exciton diffusion and separation, and the effectiveness of charge transport to the electrodes. Control of the morphology across lengthscales, spanning the range from the molecule to the several hundred nm, is critical to optimization of solar cell functionality. We control the morphology by using tailored substrate templates on which we assemble ultrathin films with well-defined regions of acceptor and photoabsorber molecules. This approach enables us to measure the morphology and interface structure with atomic resolution with scanning probe methods, and to subsequently investigate the photocurrent distribution. A pattern with variable geometry is written on the surface of highly oriented pyrolitic graphite (HOPG), our model surface, with a focussed ion beam (Ga+, 30 keV ion energy), which creates regions with a high density of surface defects interspaced with largely undamaged graphite surface. The surface defect structure, its extension and density within the pattern is characterized prior to molecule deposition. Surface defects interact strongly with the fullerene molecules, and thus provide nucleation centers for the formation of fullerene islands whose position is in registry with the artificial pattern. The boundary of the ion damaged region serves as the primary nucleation center for the formation of C60 islands, whose shape is controlled by the pattern geometry and the diffusion length of the molecules. We will describe how the artificial pattern can be used to tailor the morphology across lengthscales and discuss the extension of this method to other, technically relevant surfaces such as quartz which possesses a natural patterning in the form of ledges. The complete 2D nanostructure can be built by deposition of fullerene on the templated HOPG, and the remaining "empty" graphite surface is then filled with photoabsorber molecules. We will show the movement of porphyrin molecules into the pattern, and how the interfacial region between fullerenes and porphyrins evolves, and discuss the resultant morphologies. This hierarchical assembly of organic solar cells will enable us to tailor morphologies and link them uniquely to the photophysical processes.

9:40am **EN+EM+NS+P+A+T+V-ThM6 Photoemission Studies of Lead Sulfide Nanocrystals in Organic Films**, ***A.T. Wroble***, *D.J. Asunskis, A.M. Zachary, I.L. Bolotin,* University of Illinois at Chicago*, D.J. Wallace, M. Severson,* University of Wisonsin-Madison*, L. Hanley*, University of Illinois at Chicago

Lead sulfide (PbS) nanocrystals have shown potential for use in optoelectronic applications including photovoltaics. PbS nanocrystals are grown directly into polymers or organic oligomer matrices to control the size and surface chemistry of the resulting nanocrystals. Transmission electron microscopy is used to determine the size distribution of PbS nanocrystals in organic films grown by either colloidal synthesis in polymer solutions or gaseous deposition using a cluster beam deposition source. Both the colloidal and cluster beam deposition methods are described in detail. Various techniques in photoemission spectroscopy are then applied to these PbS nanocrystal-organic films. X-ray photoelectron spectroscopy (XPS) confirms that PbS nanocrystals are present. Soft-XPS using 200 eV photon energies available at a synchrotron radiation source provides surface sensitivity to observe the interaction of the PbS nanocrystal surface with the organic matrix and is compared to XPS results obtained using 1487 eV photon energy. Little or no bonding between the PbS nanocrystals and the organic phase is observed. The core of the nanocrystals are found to be 1:1 Pb:S, but their surfaces are enriched in Pb. Finally, core level binding energy shifts in XPS under simulated solar irradiation are used for contact-free evaluation of element-specific photovoltaic electrical response of these PbS nanocrystal-organic thin films.

10:40am **EN+EM+NS+P+A+T+V-ThM9 Rational Design of Nanostructured Hybrid Materials for Photovoltaics**, ***S.B. Darling***, *I. Botiz,* Argonne National Laboratory*, S. Tepavcevic, S.J. Sibener,* The University of Chicago*, T. Rajh, N. Dimitrijevic*, Argonne National Laboratory

Efficient conversion of photons to electricity in organic and hybrid materials depends on optimization of factors including light absorption, exciton separation, and charge carrier migration. Bulk heterojunction devices target these processes, but disorder on the nanoscale results in inefficiencies due to exciton recombination and poor mobility. By rationally designing the morphology at appropriate length scales, one can enhance the effectiveness of internal processes and, therefore, the performance of photovoltaic devices. In this work, we have implemented this approach in two hybrid material systems—both of which may provide pathways to low-cost, large-area fabrication.[1] The first involves a rod-coil block copolymer which is used both as an optoelectronically active material and as a structure-directing agent to pattern active material into ordered nanostructures. The second system uses electrochemically prepared titania nanotube arrays in concert with in situ polymerization of electron-donating material. In both cases, the characteristic donor-acceptor length scale is controlled to be comparable to the exciton diffusion length throughout the active layer, and the domains are oriented perpendicular to the incident light direction to encourage efficient charge migration.

[1] Use of the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract #DE-AC02-06CH11357. Parts of this work were also supported by the NSF-MRSEC at the University of Chicago.

11:00am **EN+EM+NS+P+A+T+V-ThM10 Electronic Energy Level Alignment in Dye Sensitized Oxide Surfaces**, ***S. Rangan***, *J.P. Theisen, E. Bersch, R.A. Bartynski*, Rutgers University

We have used direct and inverse photoemission to measure the occupied and unoccupied electronic states of N3 dye and determine their alignment with the band edges of single crystal and nanostructured TiO_2 and ZnO substrates. In dye-sensitized solar cell applications, the HOMO-LUMO gap of the dye molecule determines the useful portion of the solar spectrum, and charge transfer of photoexcited electrons to the substrate depends on the alignment of the LUMO to the substrate conduction band edge. We have compared the N3 dye properties on well characterized rutile TiO_2(110) and wurtzite ZnO single crystal surfaces to adsorption on more technologically relevant TiO_2 anatase nanoparticle and ZnO nanorod substrates. Samples were prepared and passivated with a pivalate layer in UHV, then sensitized ex-situ in a solution of N3 dye in acetonitrile. STM measurements show that the pivalic acid forms an ordered overlayer on the TiO_2(110) surface and that the N3 dye molecules can be imaged after sensitization. For N3 on TiO_2(110) as shown below, our spectroscopic measurements show that passivation significantly reduces contamination (presumably from water in the ambient) and that the N3 HOMO occurs at 0.9 eV above the TiO_2 valence band edge, while the LUMO is found 0.5 eV above the conduction band edge. On ZnO , the N3 HOMO occurs at 1.3 eV above the ZnO valence band edge but the N3 LUMO occurs 2.1 eV above the conduction band edge, much higher than what is measured on TiO_2. Comparison with experimental and theoretical values from the literature will be discussed.

11:20am **EN+EM+NS+P+A+T+V-ThM11 Preparation of Nanoporous ZnO Photoelectrode using PEG Template for the Fabrication of Dye-Sensitized Solar Cells**, ***M.F. Hossain***, *S. Biswas, M. Shahjahan, T. Takahashi*, University of Toyama, Japan

Recently, great attention has been paid to dye-sensitized solar cells (DSCs) due to their low fabrication cost. The high light-to-energy conversion efficiencies achieved with dye sensitized solar cells (DSCs) may be attributed to the nanoporous TiO_2 electrode. Zinc oxide (ZnO) is a wide band gap semiconducting material with a similar band gap and electron affinity to those of TiO_2 and has been considered as an alternative material in DSCs applications. Among the various techniques for the preparation of ZnO photo-electrode, the relatively simple sol gel method is the most widely used because of its ability to obtain films with tailored properties on large, curved substrates. In our present study, the nanoporous ZnO films were deposited on SnO_2:F coated glass by sol–gel technique with polyethylene glycol (PEG) as organic template, $Zn(CH_3COO)_2.2H_2O$ as precursor, ethanol as solvent and $NH(C_2H_2OH)2$ as chelating agent. The ZnO films have been characterized by the TG-DTA, XRD, SEM AFM, FTIR and UV-VIS systems. The surface morphology of the nanoporous ZnO films strongly depend on the $Zn(CH_3COO)_2$ concentrations, PEG contents and number of coatings. It was revealed from optical study that the dye absorption increases with the increase of PEG concentrations. Incident photon-to-current conversion efficiency is calculated for all the solar cells with different ZnO thin films to evaluate the economic viability of this technique. The variation of photoelectric conversion efficiency of the solar cells, deposited with different $Zn(CH_3COO)_2$ and PEG concentrations are discussed with the analysis of different microstructure of the ZnO thin films and the corresponding dye-incorporations.

11:40am **EN+EM+NS+P+A+T+V-ThM12 Metal / Polymer Interfaces: Ca on Polyfluorenes**, ***J.A. Farmer***, *J.H. Baricuatro,* University of Washington, *E. Zillner,* Universitaet Erlangen-Nuernberg, Germany, *J.F. Zhu,* University of Science and Technology of China*, C.T. Campbell*, University of Washington

Conjugated polymers are being investigated for use in organic photovoltaic devices and organic electronics due to favorable cost and ease of processing compared to devices based on inorganic materials. The synthetic tunability of polymer-based devices makes them applicable to many technological applications. The creation of cheap organic photovoltaic devices would significantly improve our ability to harness solar energy and curb the use of fossil fuels. The development of organic LED and organic electronics may give rise to flexible computer displays and hardware that could revolutionize human interaction with computing devices. Crucial to the performance optimization of these devices is understanding the interaction between the metal electrodes and the polymer. The structure and energetics of the interface between Ca and two polyfluorenes, poly(9,9-di-n-hexylfluorenyl-2,7-diyl) (PDHF) and poly(9,9-di-n-hexylfluorenyl-2,7-vinylene) (PDHFV), were studied in ultrahigh vacuum using adsorption microcalorimetry, and low-energy ion scattering spectroscopy. The initial sticking probabilities of Ca on pristine PDHF and PDHFV at 300 K were 0.40 and 0.53, respectively. The sticking probability of Ca on PDHFV began decreasing after ~0.06 ML, and then increased toward unity after ~0.24 ML. Because no similar behavior was seen on PDHF, this decrease in the Ca sticking probability on PDHFV is tentatively ascribed to the presence of the vinyl group. At submonolayer coverages on both polymers, the integrated Ca ISS peak area increased slowly below 1 ML, with a value less than 1 % of a saturated Ca surface at 300 K. These results indicated that most of the Ca at low coverages were below the surface, and not visible to ISS. Beyond 1 ML the Ca peak area increased, and ultimately a continuous Ca film formed at ~50 ML. Based on the variation of Ca peak area with coverage, Ca grows as 3D islands on these polymer surfaces. The heat of adsorption of Ca on PDHF at 300 K was initially 240 kJ/mol and 315 kJ/mol on PDHFV. The heat of adsorption of Ca on PDHF decreased to the heat of sublimation of Ca in ~0.25 ML; the heat of sublimation was reached by ~0.50 ML for PDHFV. The interesting thermodynamic and sticking behavior below 0.50 ML, where Ca is interacting strongly with specific adsorption sites on the polymer will be discussed, and related to the use of these polyfluorenes in device applications.

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