

Applied Surface Science

Room 324/325 - Session AS-TuM

Image Analysis and Polymer Characterization

Moderator: F.A. Stevie, North Carolina State University

8:40am **AS-TuM2 Advances in Chemical Imaging: NanoSAM and NanoESCA**, *J. Westermann, G. Schaefer, D. Funnemann, M. Maier*, Omicron NanoTechnology, GmbH, Germany

Electron spectroscopy has been a proven tool for scientific applications for decades. Challenging new applications are emerging from the fields of semiconductor and nanotechnology research and a key issue for these areas is the non-destructive imaging of sensitive structures with nanoscale dimensions. Characterization of their chemical composition and electrical properties goes hand in hand with this. We report on the development of two novel electron microscopes for chemical imaging that meet these requirements, especially for lateral image resolution in the nanoscale range. I. NanoSAM We present electron optical concepts and first results of a truly UHV compatible SEM column designed to meet the requirements for high-resolution with high beam currents. Performance checks on nanostructured samples demonstrate spot sizes below 3 nm at 15 keV beam energy and better than 5 nm at 3 keV, with sample currents being suitable for Auger electron analysis. Latest static Auger and SAM results, demonstrating the outstanding spatial resolution, will be shown. II. NanoESCA We present a parallel imaging electron microscope with an integrated high-resolution energy filter for Imaging XPS. It consists of a Photo Emission Electron Microscope (PEEM) with a large angular acceptance and an aberration corrected energy filter. The microscope allows for imaging with chemical contrast (Imaging ESCA) by energy filtering of photoelectron images. The analyzed energy of the photoelectron images ranges from threshold photoemission to 1600 eV. The instrument has been characterized with laboratory and synchrotron excitation sources. The spatial resolution limit measured so far in imaging ESCA mode is about 150 nm. The measured energy resolution follows the theoretical calculations. We show XPS spectra and energy filtered image series (video sequences) of: AlGaAs heterostructures, microstructured Au/Si and Ag/Ta samples.

9:00am **AS-TuM3 Correlation of XPS and AFM Images for Polymer Blends**, *J. Farrar, K. Artyushkova, J.E. Fulghum*, University of New Mexico; *F. Xu, N. Bantan, J. Khan*, Kent State University

Multi-technique analysis of heterogeneous polymer samples, based on AFM and XPS imaging, will provide a more complete picture of the sample under study than either technique alone. AFM provides both topographical and phase contrast information on the nanometer scale, but no chemical information is provided. Imaging XPS provides elemental and chemical information on the micron scale. A method to chemically identify the observed phases in AFM through correlation with quantitative XPS imaging will be discussed. Correlating the data from both techniques involves resizing, image alignment, resolution matching, and classification methods. The approach will be applied to a patterned polymer surface of known properties for validation and then to heterogeneous polymer blends of polystyrene/polybutadiene for phase identification. This project represents one aspect of the Active Knowledge Mesh Model (AKM) that is currently under development in our laboratories. AKM is a comprehensive image analysis system that integrates data from different techniques into a realistic three-dimensional model, visualizing structure and morphology, in multicomponent heterogeneous samples. This work has been partially supported by NSF ALCOM (DMR89-20147), NSF CHE-0113724, NSF IGERT CORE and UNM.

9:20am **AS-TuM4 XPS and Confocal Microscopy Data Fusion for Polymer Characterization**, *K. Artyushkova, J.E. Fulghum, J. Fenton, J. Farrar*, The University of New Mexico; *J. Khan, F. Xu, N. Bantan*, Kent State University

Advances in materials development require a three-dimensional characterization of complex polymeric samples in terms of both chemical structure and morphology over feature sizes ranging from nanometers to millimeters. Correlating information from multiple techniques is one method for the development of a comprehensive 'picture' of the material under study. New opportunities for multi-technique correlations arise from the improved spatial resolution and decreased acquisition times now available in a variety of imaging methods. Imaging XPS and confocal microscopy (CM) are complementary techniques that, in combination, allow for the visualization of the internal structure of heterogeneous

polymer samples. Quantitative chemical information that is readily available from the surface sensitive XPS images and spectra will be used to extract quantitative data from confocal images, which are acquired from different depth levels throughout the sample. The XPS and CM data sets can then be 'fused' to provide a surface-to-bulk visualization of changes in polymer chemistry. This work has been partially supported by NSF CHE-0113724 and NSF IGERT CORE program.

9:40am **AS-TuM5 Solvent Enhanced Surface Modification of Polymers Accompanying AFM Tip Induced Mechanical Stresses**, *F. Stevens, R. Leach, J.T. Dickinson*, Washington State University

The response of thin polymer films and bulk surfaces to combined stress and solvent is important for applications such as protective barriers (e.g., various wrappings), in controlled drug release from polymer hemispheres, resists for lithography, and nanometer scale surface modification. Over a wide range of normal forces, when a polymer is scanned by an AFM tip in contact mode in a solvent, material is not worn away, but rather the polymer surface expands forming a nanometer scale "protrusion" at and surrounding the scanned location. Furthermore, for sub-micron scan areas one observes a series of parallel ridges (moguls) perpendicular to the fast scan direction. Previous reports of the formation of raised material have nearly all been in air, required long times or very high forces to form; little evidence has been presented for the mechanism of formation. We have made a detailed study of protrusion formation and raised ridges using poly(methyl methacrylate) in alcohol based solvents. In addition to scanning in air, we have scanned the polymer surface of several molecular weights in four solvents with dramatic differences in response. We present evidence that both plastic deformation and tip induced swelling play major roles in the observed polymer surface modification by AFM. Extending this work, we have added temperature as a parameter, performing the tip stimulation at temperatures from 0 - 120 C. Major changes in the structures formed occur at higher temperatures due to increased solvent mobility and polymer mechanical properties with temperature.

10:00am **AS-TuM6 SF5+ Ion Beam Damage of Poly(Acrylates) Studied using Time of Flight Secondary Ion Mass Spectrometry**, *M.S. Wagner, G. Gillen*, National Institute of Standards and Technology

Recent advancements in instrumentation for Secondary Ion Mass Spectrometry (SIMS) have focused on the development of polyatomic primary ion sources. Polyatomic ions have been shown to increase the secondary ion yields of molecular ions from organic materials when compared with monoatomic ions of similar mass. Furthermore, some polymer films, notably poly(methyl methacrylate) and poly(ethylene glycol), display the unusual characteristic of maintaining their characteristic molecular ion signals after extended polyatomic ion bombardment. This study focuses on the effect of the chemical structure of the polymer on its stability under extended SF5+ ion bombardment. The damage of spin cast polymer films by 5 keV SF5+ was studied using positive and negative ion static Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS). A class of poly(acrylate) polymers with systematic changes to the monomer structure were investigated to determine the effects of polymer structure on the stability of their characteristic ion signals under 5 kV SF5+ bombardment in the ion dose range from 2.5 x 10@super 13@ - 5 x 10@super 14@ SF5+ ions/cm@super 2@. Preliminary results have shown that poly(methacrylic acid) and poly(methyl methacrylate) were stable under extended SF5+ bombardment while poly(methyl acrylate) was not, suggesting a role for the methyl group on the central carbon in the stabilization of the polymers under SF5+ bombardment. Monte Carlo calculations using the SRIM software@footnote 1@ show that the penetration depths of fluorine and sulfur ions in these polymers were the same despite the different damage characteristics, highlighting the importance of the chemical structure of the polymer on its stability under polyatomic ion bombardment. This study describes the breadth of applicability of SF5+ sputtering to the depth profiling of polymer films. @FootnoteText@ @footnote 1@ More information on this program can be found at <http://www.srim.org>.

10:20am **AS-TuM7 Time-of-Flight Secondary Ion Mass Spectrometry of Ordered Polymeric Monolayers: Effect on Tertiary Structures**, *J.A. Gardella, Jr., R. Rey-Santos*, State University of New York at Buffalo

The study of polymer surface structures has become an important topic in surface chemistry. Poly(dimethylsiloxane) (PDMS) plays very important roles in biological and pharmaceutical applications. A similar study of poly(methylmethacrylate) published by Nowak et al in Analytical Chemistry in 2000 was used as a model. Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) is one of the most powerful techniques for

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polymer study. TOF-SIMS was used to study the fragmentation mechanism of this polymer. Using a statistical chain breaking model of PDMS helped us to understand the fragmentation pattern obtained in the spectra. The Langmuir-Blodgett (LB) technique helps us to prepare a molecular monolayer at the air/water interface. The LB technique was used to prepare well-ordered monolayers. Reflection Absorption Fourier Transform Infrared Spectrophotometry (RA-FTIR) is an ideal technique for surface study to obtain information about molecular structures. It has been used to compare results from amorphous, solution cast films to that from ordered, LB films of PDMS. An ion formation mechanism for PDMS was investigated to get information of the long-range forces between polymer chains.

10:40am **AS-TuM8 Grazing Incident X-ray Diffraction Study of Poly(alkylthiophene) Thin Films on Various Substrates**, *M. Morita, T. Koga, H. Yakabe, S. Sasaki*, Kyushu University, Japan; *O. Sakata*, JASRI, Japan; *A. Takahara*, Kyushu University, Japan

The crystalline aggregation states of organic semiconductor molecules in thin films might play an important role in the performance of organic semiconductors. The purpose of this study is to reveal the crystalline orientation and crystallinity of spin-coated poly(3-hexylthiophene)[P3HT] on Si-wafer substrate at the near-surface region and internal phase. The surface crystalline states of P3HT thin film were studied with synchrotron radiation in-plane grazing incidence x-ray diffraction GIXD. Surface modification of Si-wafer with perfluorohexylethyltrimethoxysilane prior to P3HT coating resulted in the preferential orientation with the alkyl side chains normal to the substrate surface. In contrast, the surface modification of Si-wafer with vacuum ultraviolet(VUV)-ray with wave length of 172nm or n-octadecyltrimethoxysilane resulted in the orientation with the alkyl side chains parallel to the substrate.

11:00am **AS-TuM9 Study of Water-Induced Reorganization of Amphiphilic Graft Copolymers Containing Poly(2-hydroxyethyl methacrylate) and Polydimethylsiloxane by Angle-dependent X-ray Photoelectron Spectroscopy**, *L. Chen*, State University of New York at Buffalo; *A.P. van Bavel*, Eindhoven University of Technology, The Netherlands; *J.A. Gardella*, State University of New York at Buffalo

The free air surface composition and water-induced reorganization of a series of amphiphilic graft copolymers consisting of hydrophilic poly(2-hydroxyethyl methacrylate) [poly(HEMA)] backbones and hydrophobic poly(dimethylsiloxane) (PDMS) side chains prepared by both photoinduced-radical and anionic polymerization techniques were studied by angle-dependent X-ray Photoelectron Spectroscopy (XPS). Copolymers with broad molecular weight distributions (MWD; e. g. Mw/Mn = 3.0) were prepared by the radical copolymerization technique. Copolymers with narrow MWD (e. g. Mw/Mn = 1.1) were prepared by the anionic copolymerization technique. The free air surface composition of copolymers was studied as a function of MWD, PDMS bulk content and PDMS graft length. It was found that anionically prepared copolymers with narrow MWD have higher PDMS surface concentration than radically prepared copolymers with broad MWD. PDMS surface concentration increased with increasing PDMS bulk content. For a given PDMS bulk content, a longer PDMS graft chain gave a surface richer in siloxane. The water-induced reorganization of copolymers was studied as a function of MWD, PDMS graft length and water exposure time. The dry films were exposed to water (hydration) and then frozen in a nitrogen gas purge to preserve the surface composition during XPS analysis. The XPS results showed both MWD and PDMS graft length influenced the extent of the graft chain reorganization at the surface.

11:20am **AS-TuM10 The Role of Polymer Architecture and Environmental Humidity on the Interfacial Conformation and Properties of Surface-adsorbed Poly(L-lysine)-graft-poly(ethylene Glycol) Co-polymer**, *F. Assi, S. Pasche, L. Feuz, N.D. Spencer, M. Textor*, ETH Zurich, Switzerland

The development of protein-resistant surfaces is of central interest in the context of biosensor chip development and for the design of medical implants in contact with blood. Self-organized films of PEG based copolymers on different oxide surfaces are one system that has been investigated by a variety of surface characterization techniques in order to establish systematic correlations between the polymer composition/structure, interface architecture and interaction with protein-based biological media. A class of co-polymeric molecules of special interest is based on a poly(L-lysine) backbone, charged positively due to the presence of protonated amine groups at a neutral pH, and grafted with poly(ethylene glycol) side chains (short: PLL-g-PEG). Although the protein-resistant properties of these films have already been demonstrated, little is known about the effect of the co-polymer interfacial architecture on the

resulting protein resistance. One of the most important factors turns out to be the polymer conformation in the adsorbed state, which depends not only on the polymer architecture but also on the environment the polymer, is exposed to. We report results that elucidate the surface conformation of PLL-g-PEG of different molecular architecture at various humidity levels in air as well as in contact with aqueous solutions, studied by means of atomic force microscopy (AFM, for the polymer conformation and adhesion properties) and ellipsometry (ELM, for the layer thickness). AFM force-distance measurements in compression between a 5- μm SiO₂@sub 2@ sphere and a PLL-g-PEG-coated substrate showed a good correlation with the architecture of the polymer. Furthermore, tensile-mode (pull-off) AFM studies were used to quantify the adhesion strength level of the polymeric molecules at oxide surfaces. The experimental results for different polymers were finally compared to the results of self-consistent field calculations.

11:40am **AS-TuM11 Ultra-fast Laser Ablation as a Facilitator for Depth-dependant Characterization of High Pigment Volume Concentration Organic Coatings**, *L.T. Keene, C.R. Clayton, G.P. Halada, T. Fiero*, State University of New York at Stony Brook

The strong dielectric nature of most organic coatings, particularly those used on an industrial scale, presents the scientific investigator considering a depth-profiling approach to chemical characterization of such organic coatings with a serious challenge. The ultra-fast optical phenomenon of femtosecond laser ablation presents one possible solution to such a problem. An apparent athermal, non-selective ablation process becomes possible when the pulse temporal scale reaches the femtosecond (10⁻¹⁵ s) level. This remarkable property of femtosecond-class lasers enables the multi-layer removal of organic/inorganic composite coatings for the purpose of chemical characterization as a function of coating depth. If proven experimentally, this capability becomes attractive when considering the depth-analysis of materials that demonstrate either strong dielectric properties (and, hence, resist depth profiling via traditional charged particle beam methods) or are chemically inhomogeneous in nature (which generally cause problems such as selective sputtering). This talk will focus on the experimental use of ultra-fast laser ablation for the facilitation of depth-profiling high solids organic coatings with particular emphasis placed on military application two-component solvent-based polyurethane coatings containing a variety of inorganic pigments and fillers. The high dielectric and chemically inhomogeneous natures of these coatings pose a demanding application for uniform laser removal without chemically modifying the host material. Cross-sectional analysis of the materials via Scanning Electron Microscopy (SEM) / Energy Dispersive Analysis of X-rays (EDS) will be shown. Ablation of the aforementioned materials was conducted both in atmosphere as well as high vacuum. Chemical modification of host material due to the ablation process will be discussed via the results of Fourier Transform Infrared Spectroscopic analysis of ablated material before, and after, ablation. Morphological features of ablated regions collected via high-resolution scanning confocal profilometry as a function of the processing parameters, and how these features limit the removal depth resolution, will be shown. S. McKnight, J. Beatty, Mechanisms of Military Coatings Degradation, ARL Weapons & Materials Directorate, (1999) 1. C.R. Hegedus, et. al., "A Review of Organic Coating Technology for U.S. Naval Aircraft," Journal of Coatings Technology, Vol. 61, No. 778, pp 31-42, (1989) 3. L. Keene, G. Halada, C. Clayton, S. McKnight, W. Kosik, "Novel Techniques for the Investigation of Long-term Photodegradation of Multi-layer Polymer Coatings," in State-Of-The-Art Application of Surface and Interface Analysis Methods, The Electrochemical Society Proceeding Series, Pennington, NJ, (199th Electrochemical Society Meeting; Washington D.C.) (2001) 4. A.A. Serafetinides, M.I. Makropoulou, C.D. Skordoulis, A.K. Kar Appl. Surf. Sci. 42-56 (2001) 180

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