

# Wednesday Afternoon, October 17, 2007

## Applied Surface Science

Room: 610 - Session AS+BI+NS-WeA

### Fabrication and Characterization of Functional Soft Material Surfaces

**Moderator:** R.T. Haasch, University of Illinois at Urbana Champaign

1:40pm **AS+BI+NS-WeA1 UPS Work Function Measurements on Polymers Combined with C60 Depth Profiling.** *S. Raman, J. Moulder, J.S. Hammond*, Physical Electronics, *N. Sanada, M. Suzuki*, ULVAC-PHI, Inc.

The performance of ultra thin organic films in organic LED's (OLED) is dependent on the work functions of the electrodes and polymers forming the OLED junctions. Historically, the work functions have frequently been derived from the secondary electron emission edges measured with UPS. The recent applications of C60 ion beams for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage, have offered a new tool for studying surface modified polymers. By combining these two techniques, the work function and composition as a function of depth of polymers targeted for OLED applications can be characterized by XPS and UPS. The surface characterization of OLED component polymers exposed to deleterious environments will also be discussed. The possible chemical surface damage induced by the C60 ion beams will be examined by both XPS and UPS spectra and secondary electron emission edge spectra.

2:00pm **AS+BI+NS-WeA2 Patterning and Bonding of Poly(dimethylsiloxane) A Simple New Method for Creating Optically Transparent Biocompatible Surfaces and Robust Microfluidic Devices.** *P.R. Norton, N. Patrio, J. McLachlan, J. Chan, S. Faria, S. Tadayyon*, University of Western Ontario, Canada

Our group has developed a simple protocol to prepare inexpensive, single-component substrates capable of confining cell attachment and growth. In the presence of an argon plasma, thin metal films are deposited onto poly(dimethylsiloxane) (PDMS). Removal of the metal layer exposes regions of the polymer surface that are enriched in oxygen and promote the adhesion of fibroblast, epithelial and myoblast cells. This method produces bioactive arrays of controlled size (down to scales in the order of  $\mu\text{m}$ ), shape, pitch and symmetry on which cells can be grown to confluency. The treated material is storable and can be activated just before use; this eliminates stability problems inherent in a number of previously reported PDMS surface treatments, most notably oxygen plasma modification. The patterned arrays offer highly adaptable means to probe cell-cell interactions, cell motility and cell signaling in response to varied spatial or geometric organization and they are being incorporated into microfluidic channels for combined optical and proximal probe studies of live cells. Serendipitously, this surface treatment alters the mechanical properties of PDMS, rendering the modified material sensitive to tensile stresses imposed by cells. Cellular traction forces generate nanoscale ripples in the elastic substrata which extend outward from the cell bodies and which can be imaged by dark-field microscopy and AFM. Detailed analyses of these ripples can potentially provide a direct measure of cellular traction forces and mechanical signaling. In related experiments, we have also developed a novel means of bonding PDMS to a host of materials relevant to microfluidic device fabrication, including glass, Si, SiO<sub>2</sub> and polystyrene. To quantify the adhesive strength, closed PDMS-glass and PDMS-PDMS microfluidic devices were fabricated and subjected to tensile and leakage testing. The data indicate a significant improvement in performance over previously reported bonding technologies, resulting in the production of more robust, longer-lasting microfluidic devices and the concomitant possibility of using higher pressures and flow-rates.

2:20pm **AS+BI+NS-WeA3 Interfacial Structure of Polymer Brush and Gel Investigated by Sum Frequency Generation Spectroscopy.** *K. Uosaki, H. Noguchi, S. Nihonyanagi, H. Minowa, R. Yamamoto*, Hokkaido University, Japan

Polymer brush and gel plays very important roles in biological systems. Information on the interfacial structure is essential to understand the function of these materials. Here we employed sum frequency generation (SFG) spectroscopy, which is known to possess high surface specificity, to investigate the molecular orientation/conformation of polymer brush under

various environment and water structure at PVA gel/solid interface. SFG spectra of alkylated poly (vinyl pyridine) in contact with dry nitrogen, water vapor, and liquid water were obtained. The peaks due to CH vibration of CH<sub>3</sub> dominated in nitrogen, showing that the side chains are highly ordered. When the polymer layer is in contact with water vapor, in addition to the two peaks due to CH<sub>3</sub> group, two peaks of CH<sub>2</sub> group were observed, indicating that many gauche defects existed. The SFG spectrum of the polymer brush in contact with liquid water showed no peaks in CH stretching region except for small shoulder due to the ring CH modes, indicating the alkyl side chain was completely disordered. SFG spectra of the polymer brush in OH stretching region were also obtained. A broad band assigned to the OH stretching was observed in water vapor. Two bands corresponding to the OH stretching of the interfacial water molecules at 3200 cm<sup>-1</sup> due to "ice-like water" and at 3400 cm<sup>-1</sup> due to "liquid-like water" dominated in liquid water. Poly vinyl alcohol (PVA) gel is considered to be one of the possible candidates for an artificial articular cartilage in artificial joints because of very low friction between PVA gel and solid. SFG measurement proved that while the fractions of the "ice-like" and "liquid-like" water were almost equal at water/quartz interface, the fraction of the "liquid-like" water became much higher when the PVA gel was pressed against the quartz surface, showing that the weakly hydrogen bonded water dominate at PVA gel/quartz interface where friction is very low. SFG measurement in Ar showed only weakly hydrogen bonded water was present at the PVA gel/quartz interface. The effect of PVA gel contact was less obvious at the octadecyltrichlorosilane (OTS) coated quartz, where the friction is much higher. These results suggest the important role of weakly hydrogen bonded water for very small friction at PVA gel/solid interface. In conclusion, SFG is demonstrated to be a very useful technique to characterize molecular structure at solid/liquid interfaces including biological interfaces.

2:40pm **AS+BI+NS-WeA4 Multiphoton Patterning of Planar and Topographically Complex Surfaces for Control of Photon, Electron, and Chemical Transport.** *P.V. Braun*, University of Illinois at Urbana-Champaign **INVITED**

Multiphoton patterning enables fabrication of complex structures with minimum feature sizes on the order of the volume of the focal point. Using a pulsed laser source coupled to a laser scanning confocal microscope, we have concurrently written and imaged various complex structures and patterns. Recently, along with formation of complex structures, we have initiated efforts to locally modify the surface chemistry of both planar and topographically complex (three-dimensional) surfaces to create pathways for photon, electron, and chemical transport. A series of organic chemistries have been developed to enable this patterning, which revolve around the grafting of photoswitchable molecules or polymer brushes to the various surfaces. Once the local chemistry of the surface has been modulated, this chemistry can be amplified through quantum dot attachment, electroless plating, or surface initiated polymerization to create two and three-dimensional patterns for control of photon, electron, and chemical transport. Colloidal crystals and porous glasses are used as model three-dimensional substrates; standard materials are used for two-dimensional structures.

4:00pm **AS+BI+NS-WeA8 Chemical Modification of Self-Assembled Monolayer Surfaces using Soft-Landing of Mass-Selected Ions.** *P. Wang, O. Hadjar, J. Laskin*, Pacific Northwest National Laboratory

Stable immobilization of peptides on solid supports plays an important role in biochemistry. Existing techniques for linking peptides to surfaces are based on a variety of solution-phase synthetic strategies and require relatively large quantities of purified material. Here, we report a novel approach for preparation of peptide arrays on self-assembled monolayer (SAM) surfaces using soft-landing (SL) of mass-selected ions. This approach takes advantage of the exceptional selectivity in preparation of projectile ions by mass spectrometry. We demonstrate efficient reactive landing (RL) of several model peptides onto the SAM of N-hydroxysuccinimidyl ester terminated alkylthiol on gold (NHS-SAM). This method introduces unprecedented selectivity and specificity into the surface preparation step by eliminating the effect of solvent and sample impurities on the quality of the film. Peptide ions produced by electrospray ionization are mass-selected and deposited onto SAM surfaces using a novel ion deposition chamber designed and constructed in our laboratory. NHS-SAM, which readily reacts with accessible primary amino groups in proteins or peptides by forming amide bonds, is used as a target for soft-landing experiments. Freshly prepared SAMs and modified surfaces are characterized ex situ using time-of-flight secondary ion mass spectrometry (ToF-SIMS) and infrared reflection absorption spectroscopy (IRRAS). Mass-selected ions of model peptides including cyclo(-RGDfK-), GRGDSPK and RGDGG were soft-landed onto the NHS-SAM surface.

ToF-SIMS and IRRAS characterization suggested efficient covalent binding between the two lysine-containing peptides and the NHS-SAM by the formation of an amide bond through the lysine side chain. Systematic studies were carried out to understand the factors that affect the efficiency of reactive landing. We found that the reaction takes place upon collision and is promoted by the kinetic energy of the ion. The reaction yield is independent of the charge state of the projectile ion suggesting efficient neutralization of peptide ions upon collision. Chemical reactivity and physical properties of the SAM surface are also important factors that affect the outcome of RL. RL of mass- and energy-selected peptide ions on surfaces provides a highly specific approach for covalent immobilization of biological molecules onto SAM surfaces.

4:20pm **AS+BI+NS-WeA9 TOF-SIMS Analysis of Polypropylene Films Modified by Isotopically Labeled Methane Flames.** *S.J. Pachuta, M.A. Strobel*, 3M Company

Flame treatment is a common industrial process for modifying polymer surfaces. Surfaces exposed to flames are known to oxidize, but studies of the oxidation mechanism have been largely confined to correlating simple surface properties with models of the flame composition due to the lack of direct experimental data on the flame-surface interaction. In this work, polypropylene film surfaces were oxidized by exposure to a flame fueled by isotopically-labeled methane (CD<sub>4</sub>). The isotopic sensitivity of time-of-flight secondary ion mass spectrometry (ToF-SIMS) was then used to gain new insights into the mechanism of flame treatment. TOF-SIMS analysis indicates that much of the oxidation of polypropylene occurring in fuel-lean flames is not accompanied by deuteration, while for polypropylene treated in fuel-rich flames, deuteration is extensive, and some of the affixed oxygen is deuterated. These observations imply that O<sub>2</sub> is the primary source of affixed surface oxygen in fuel-lean flame treatments, but that OH may be a significant source of affixed oxygen in fuel-rich flame treatments. Application of principal component analysis (PCA) and multivariate curve resolution (MCR) to the TOF-SIMS data was found to provide information beyond that which could be obtained by traditional peak-ratio methodology.

4:40pm **AS+BI+NS-WeA10 The Analysis of Oxidation Profiles in Elastomers Using ToF-SIMS.** *J.A. Ohlhausen, M.C. Celina, M.R. Keenan*, Sandia National Laboratories

As elastomeric materials age, their mechanical properties can change such that they do not perform their desired function. It is important to understand the aging behaviour of such elastomers, so that predictive aging models can be developed. In that light, much work has been done to understand oxygen diffusion limited aging processes under accelerated aging conditions for a range of elastomers.<sup>1,2</sup> In these studies, mechanical properties as a function of depth were determined under differing temperature/time conditions. In addition, chemical changes were measured by analyzing microtomed sections using FTIR. Unfortunately, these measurements were difficult to perform on carbon-black filled samples and were also relatively time consuming. Ideally, an alternative method is needed to measure the chemical oxidation profiles of commercial o-rings containing fillers in a quick and efficient manner. In this talk, the usefulness of ToF-SIMS as a technique to measure the position-dependent extent of oxidation in filled elastomers will be discussed. Accelerated aging in 18O is used to demonstrate the ability of SIMS to directly measure the extent of oxidation. Examples of 18O- cross section line scans in aged elastomers will be discussed and compared to known diffusion limited degradation mechanical profiles. It will be shown that filled elastomers can be analysed using these methods. Additionally, the ability to measure oxidation profiles in air-aged samples will also be shown. Thus, ToF-SIMS is seen as a rapid evaluation tool for the measurement of elastomer oxidation for engineered elastomers. The benefits and limitations of the technique will be discussed. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

<sup>1</sup> M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, *Polymer Degradation and Stability* 60 (1998) 493-504

<sup>2</sup> M. Celina, J. Wise, D. K. Ottesen, K. T. Gillen, R. L. Clough, *Polymer Degradation and Stability* 68 (2000) 171-184 .

5:00pm **AS+BI+NS-WeA11 Surface Chemical Analysis of Nano-Scaled r.f. Plasma Polymer and Co-Polymer Films by using a Combination of "In-Situ" and Ex-Situ Characterization Tools: Hydroxylated and Aminated Surfaces by XPS, ToF-SIMS and NEXAFS Spectroscopy.** *W.E.S. Unger, A. Lippitz, S. Swaraj, E. Yegen*, Federal Institute for Materials Research and Testing (BAM), Germany

The formation of plasma-polymerized materials made from organic molecules is a technologically highly attractive way to obtain films with unique properties. Surface properties like bio-compatibility, wettability, etc., can be adjusted by tailoring the chemical functionalization. A controlled deposition of those films requires the development of surface

analytical procedures which are able to derive useful information on relevant parameters. This can be a hard job for an analyst because plasma-polymerized or plasma-modified materials are extremely complex samples. Their complexity is caused by the co-existence of a relatively high number of chemical species. This leads to a kind of mixture analysis at surfaces but without the possibility of a separation step as it is possible, e.g., by using GC-MS techniques in the analysis of organic mixtures. Relevant parameters for film characterization are primarily (1) qualitative and (2) quantitative determination of functional groups. However there are other important parameters as for instance (3) the cross-linking and branching within the films or even the concentrations of (4) radicals and (5) unsaturated species in the films. It is well known that plasma-polymerized materials may undergo ageing processes. It is assumed that many of them will be initiated by radicals in the films. These radicals are inherently produced by plasma processing. Approaches have to be developed enabling a study of ageing processes on the molecular level including the respective reaction kinetics. So-called "in-situ" techniques of surface chemical analysis are required to investigate the real fresh state of samples. Using a selection of hydroxylated or aminated model plasma polymers and co-polymers it will be demonstrated how analytical approaches based on a combination of photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS) and x-ray absorption spectroscopy (XAS) may provide solutions for the analytical challenges summarized above.

# Authors Index

**Bold page numbers indicate the presenter**

## — B —

Braun, P.V.: AS+BI+NS-WeA4, **1**

## — C —

Celina, M.C.: AS+BI+NS-WeA10, **2**

Chan, J.: AS+BI+NS-WeA2, **1**

## — F —

Faria, S.: AS+BI+NS-WeA2, **1**

## — H —

Hadjar, O.: AS+BI+NS-WeA8, **1**

Hammond, J.S.: AS+BI+NS-WeA1, **1**

## — K —

Keenan, M.R.: AS+BI+NS-WeA10, **2**

## — L —

Laskin, J.: AS+BI+NS-WeA8, **1**

Lippitz, A.: AS+BI+NS-WeA11, **2**

## — M —

McLachlan, J.: AS+BI+NS-WeA2, **1**

Minowa, H.: AS+BI+NS-WeA3, **1**

Moulder, J.: AS+BI+NS-WeA1, **1**

## — N —

Nihonyanagi, S.: AS+BI+NS-WeA3, **1**

Noguchi, H.: AS+BI+NS-WeA3, **1**

Norton, P.R.: AS+BI+NS-WeA2, **1**

## — O —

Ohlhausen, J.A.: AS+BI+NS-WeA10, **2**

## — P —

Pachuta, S.J.: AS+BI+NS-WeA9, **2**

Patrito, N.: AS+BI+NS-WeA2, **1**

## — R —

Raman, S.: AS+BI+NS-WeA1, **1**

## — S —

Sanada, N.: AS+BI+NS-WeA1, **1**

Strobel, M.A.: AS+BI+NS-WeA9, **2**

Suzuki, M.: AS+BI+NS-WeA1, **1**

Swaraj, S.: AS+BI+NS-WeA11, **2**

## — T —

Tadayyon, S.: AS+BI+NS-WeA2, **1**

## — U —

Unger, W.E.S.: AS+BI+NS-WeA11, **2**

Uosaki, K.: AS+BI+NS-WeA3, **1**

## — W —

Wang, P.: AS+BI+NS-WeA8, **1**

## — Y —

Yamamoto, R.: AS+BI+NS-WeA3, **1**

Yegen, E.: AS+BI+NS-WeA11, **2**