Wednesday Morning, November 15, 2006

Applied Surface Science
Room 2005 - Session AS-WeM

Molecular Ion Sources and Characterization of Biomaterials

Moderator: J. Shallenberger, Evans Analytical Group

8:00am **AS-WeM1 Recent Advancements in Polymeric Depth Profiling with an SF@sub 5@@super +@ Cluster Primary Ion Source**, ***C.M. Mahoney,*** National Institute of Standards and Technology **INVITED**

The utility of cluster Secondary Ion Mass Spectrometry (SIMS) for depth profiling applications in polymeric materials has been repeatedly demonstrated in the past decade, where it has been used to obtain molecular and fragment information as a function of depth in several polymer systems.@footnote 1,2,3,4@ In addition to homopolymers, polymeric blends, multilayers and copolymer systems have been successfully characterized as a function of depth.@footnote 2,4@ Finally, the capability to monitor the in-depth distribution of small molecules embedded in organic and polymeric matrices has been realized.@footnote 1,5@ This talk will describe the ongoing research efforts at NIST to further develop cluster SIMS as a tool for polymer surface and in-depth characterization. Results indicate that SF@sub 5@@super +@ is a promising tool for polymer depth profiling, and with the right set of conditions, including temperature, sample rotation and selection of analysis source, one can obtain optimal results. @FootnoteText@ @footnote 1@ Mahoney, C.M.; Roberson, S.V.; Gillen, G. Anal. Chem. 2004, 76, 3199-3207.@footnote 2@ Mahoney, C.M.; Yu, J.X.; Gardella, J.A. Jr. Anal. Chem. 2005, 77 (11), 3570-3578.@footnote 3@ Wagner, M.S. Surf. Interface Anal. 2005, 37(1), 42-70.@footnote 4@ Wagner, M.S. Anal. Chem. 2005. 77(3), 911-922.@footnote 5@ Chen, J.; Winograd, N. Anal. Chem. 2005, 77(11), 3651-3659.

8:40am **AS-WeM3 TOF-SIMS Analysis of C60 Sputtered Organic Thin Films**, ***S.R. Bryan***, *J. Moulder, G.L. Fisher,* Physical Electronics*; N. Sanada,* ULVAC-PHI

Sputtering of organic materials using a C60 ion beam has been demonstrated to produce significantly less accumulated damage compared to sputtering with atomic ion beams. This has opened up the possibility of sputtering organic materials while maintaining the organic structural integrity at the bottom of the crater. We have studied C60 sputtering for several years using XPS. This has lead to a better understanding of the optimum sputting conditions. In this presentation we will present new data on TOF-SIMS analysis of C60 sputtered organic films. By combining the quantification and atomic bonding information from XPS with the longer range structural information from TOF-SIMS, a better understanding of the C60 sputtering process will emerge.

9:00am **AS-WeM4 XPS and QCM Studies of PMMA and Teflon AF1600 Films Bombarded by 1-20 keV C@sub 60@@super +@ Ions**, *I.L. Bolotin, S.H. Tetzler,* ***L. Hanley,*** University of Illinois at Chicago

keV C@sub 60@ ions are widely used as projectiles in secondary ion mass spectrometry of polymeric materials. Evidence exists that the mechanism of sputtering by C@sub 60@ ions allows their use for damage-free depth profiling. Surface analysis studies are presented to probe absolute sputtering yields and surface modification of two polymer films by C@sub 60@ ions. Polymethylmethacrylate (PMMA) and Teflon AF1600 spin-casting films studied during different bombardment doses of C@sub 60@ ions with energies of 1-20 keV by quartz-crystal microbalance (QCM) and X-ray photoelectron spectroscopy (XPS) . Measurements for the total sputter yield of films are acquired using a QCM. Mass-lost rate data show that each 20 keV C@sub 60@ cluster leads to emission ~10@super 6@ amu of polymer, indicating that the non-overlapping crater regime exists for doses of 10 keV. Chemical modification is also probed by XPS of the target surface before and after ion bombardment. Both polymers display little to no damage to their film structure at ion fluences below ~10@super 13@ ion/cm@super 2@. Changes in C 1s XPS spectra during higher fluence bombardment can be explained predominantly by differential charging effects. However, ion fluences >10@super 15@ ion/cm@super 2@ modify the film composition to a carbon-rich material with various degradation products.

9:40am **AS-WeM6 Applications of a Bismuth-Cluster Ion Gun in Organic and Inorganic Surface Analysis**, ***F. Kollmer***, *R. Moellers, T. Grehl, D. Rading, E. Niehuis,* ION-TOF GmbH, Germany

In recent years primary ion clusters are increasingly applied for the analysis of organic surfaces by TOF-SIMS. Since they increase the secondary ion formation efficiency by orders of magnitude cluster sources are replacing the mono-atomic primary ion sources more and more. As primary ion species a large variety of different clusters as Au@sub n@, Bi@sub n@, C@sub n@, C@sub 60@, SF@sub 5@ ,...are applied. Possible drawbacks of cluster sources are the applicable cluster currents (measurement time) and the achievable performance with respect to lateral resolution and mass resolution. Recent advances in molecular surface analysis were made by the application of cluster liquid metal ion sources (LMIG) operated with Au or Bi. These sources combine the fundamental benefits of cluster ion bombardment with a high brightness source capable to achieve a high performance with respect to lateral resolution and mass resolution. In particular the Bi source shows interesting aspects as a large variety of emitted singly and doubly charged ions, high cluster currents, and the ability to operate at very low emission currents. At low emission currents the energy spread of the emitted species is reduced which improves the achievable lateral resolution. In this contribution we address fundamental capabilities of the Bi cluster source as the composition of the emitted primary ion beam, the energy spread of the ions, the stability of the source and the influence of the emission current on these. We applied Bi cluster ions to organic surfaces for micro area analysis and imaging with high lateral resolution. We also found new interesting applications of Bi clusters for inorganic surface analysis and dual-beam depth-profiling.

10:40am **AS-WeM9 Utilization of Polymers in Ocular Science Applications**, ***R.M. Braun,*** Bausch & Lomb **INVITED**

The healthcare industry, as a whole, has seen the rapid incorporation of polymeric materials into a variety of devices in recent years. This progression along the development trail has led to a multitude of life-changing products that range from convenience items like liquid bandages to prostheses that repair damaged joints and teeth. Moreover, we can not forget the life-saving products like stents and heart valves, nor the pharmaceutical products that rely on polymers to regulate dosing within a given application. Clearly, the use of polymers within biomaterial applications has become widespread and will likely continue to expand as time progresses. Although advancements in the ocular sciences industry are not often highlighted in the same light as those noted above, contributions toward improving patient health and the quality of life through materials development are abundant. These facts have recently come to light with the aging population associated with the baby-boomer generation. The products and applications within this industry include contact lenses and associated comfort solutions, replacement lenses for cataract issues and pharmaceutical products that treat back of the eye diseases that can lead to blindness. While these industry sectors are too large to discuss completely, this talk will highlight a few biomaterial related systems associated with the human eye and touch on some of the challenges associated with surface analytical measurements.

11:20am **AS-WeM11 Multi-Technique Characterization of a Drug Delivery System to Obtain 3-D Chemical Information**, ***A.M. Belu,*** Medtronic, Inc.*; C.M. Mahoney,* National Institute of Standards and Technology*; K. Wormuth,* SurModics, Inc.

Medical devices are increasingly being designed to incorporate drug delivery. For example, drugs are currently incorporated into catheters to reduce microbial infection, placed on stents to prevent restinosis of the artery, and incorporated into pacing lead tips to prevent inflammation of heart tissue. As more drug delivery systems are being created, it is important to characterize their properties, and relate the properties to how the system will function in the human body. This study focuses on the characterization of a rapamycin/PLGA delivery system on a stent. The goal is to understand the lateral and depth distribution of the drug in the polymer film. The information can then be used to predict the release profile of the drug in vivo. Several different formulations of rapamycin/PLGA were studied (5, 25, 50% drug, and 25% with a capcoat). The surface composition of the films were characterized and quantified by ESCA and TOF-SIMS. Information on drug concentration from the surface towards the bulk of the film was determined by depth profiling by SIMS with a cluster ion source. To determine the distribution of drug/polymer species in the bulk of the film in the x-, y-, and z-direction, confocal Raman was used. In the films with high concentration of drug, individual clusters of drug on the order of a few microns were resolved. The data from the multiple methods of characterization will be compiled to allow a fuller understanding of the delivery systems. The strengths and weaknesses of each of the characterization techniques will be compared.

11:40am **AS-WeM12 Combining Fluidics, Surface Chemistries and Direct Mass Spectrometric Detection to Address Protein Analyte Quantitation from Complex Samples for the Purpose of Diagnostic Assays***, L.O. Lomas,* *E. Fung, E. Boschetti,* Ciphergen

The development of analyte assays for the purpose of diagnostic tests is driven by multiple factors, including sample availability, required throughput and quantitative reproducibility. Although antibody-based assays have dominated in the detection of peptide/protein analytes and serve well in terms of throughput and quantitative reproducibility, mass spectrometry is becoming more main-stream due to the added information provided in terms of precise analyte conformation by mass and/or secondary structure fragmentation. Laser Desorption/ionization mass spectrometry (MS) is particularly well suited for both peptide and protein characterization, however, absolute quantitation has been elusive due to complexities associated with integrating sample processing and final analyte detection. To resolve these issues, we have integrated unique solid-phase extractions chemistries directly on MS probes that allow us to quantitatively extract the protein analytes of interest from a complex sample in a defined and controlled process. The resulting analyte arrays minimize the sample requirements and allow for high-throughput processing using standard sample fluidic systems. To exemplify this process, we describe the development of a seven protein-marker panel that may aid in the stratification of women with a pelvic mass. The specific MS-based analyte array assays permit the discrimination of post-translationally modified forms of the markers and by using reference standards, we are able to achieve absolute quantitation with high reproducibility (CV<10%). The integrated assay platform includes an automated liquid handler, analyte-specific arrays, and a MS reader. Measurements of the seven markers provide a measure of the risk that a pelvic mass is malignant. Women at low risk for ovarian cancer can be further evaluated by their general gynecologist, while women at high risk for ovarian cancer should be evaluated by a specialist gynecologic oncologist.

12:00pm **AS-WeM13 The Surface Characterisation of Arrayed Biomaterial Systems***, A.J. Urquhart,* University of Nottingham, UK*; D.G. Anderson,* Massachusetts Institute of Technology*; M.R. Alexander,* University of Nottingham, UK*; R. Langer,* Massachusetts Institute of Technology*; M.C. Davies,* University of Nottingham, UK

In recent years the increase in interest in combinatorial materials science, via high throughput synthetic techniques, has attracted considerable interest mainly in the facilitation of rapid discovery and the optimisation of functional polymeric biomaterials.@footnote 1@ Critical to the selection of a biomaterial to a specific clinical application is the relationship between polymer interfacial chemistry and biological response. However, there has been to date few reports addressing the challenge of studying the interfacial chemistry of high throughput arrays with high spatial resolution. Here we report, for the first time, on the surface characterisation of a novel polymer array, comprising of 572 polymer species (each polymer spot being approximately 300 µm in diameter) and fabricated by the Anderson et al. method,@footnote 1@ using X-ray photoelectron spectroscopy (XPS), time of flight secondary ion mass spectroscopy (ToF-SIMS), water contact angle (WCA) and atomic force microscopy (AFM). In order to maximise the information obtained from the large data sets principal component analysis was applied to observe trends between polymer composition and stem cell adhesion/proliferation on the arrays. @FootnoteText@ @footnote 1@ D. G. Anderson, S. Levenberg and R. Langer, Nature Biotechnology, 2004, 22, 863.

Author Index

Bold page numbers indicate presenter