Tuesday Morning, October 21, 2008

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.

Authors Index

Bold page numbers indicate the presenter