Applied Surface Science Division
Room: 102 - Session AS-TuM

Imaging and 3D Chemical Analysis
Moderator: V.S. Smentkowski, GE-GRC, X. Dong, Eli Lilly and Company

8:00am **AS-TuM1 Recent Applications of GCIB Depth Profiling with XPS and TOF-SIMS**, ***T. Miyayama***, *N. Sanada*, ULVAC-PHI Inc., Japan, *J.S. Hammond*, Physical Electronics **INVITED**

The development of new electronic devices incorporating organic materials, such as Organic Light Emitting Diodes (OLED's) and Organic Photovoltaics (OPV's) is rapidly increasing. To control quality, performance and lifetimes of these devices, it is necessary to characterize the layer structures and the dopant distributions in the thin organic materials. Conventional surface analysis techniques such as XPS and TOF-SIMS, combined with mono-atomic ion beam sputtering, have been widely used for chemical depth profiling of inorganic thin films. However, this approach has not been successful for the depth profiling of organic materials due to the loss of chemical information during the sputtering process. Recent cluster ion beam developments utilizing C_{60} and Coronene ions have also had limited success for the XPS and TOF-SIMS depth profiling of OLED and OPV structures due to similar modification of chemical and molecular information as a function of sputter depth.

The chemical depth profiling of organic layers with thicknesses greater than one micron has also been problematic utilizing XPS and TOF-SIMS with C_{60} cluster sources. The implementation of new cluster ion sources that could extend chemical depth profiling of organics to more than several microns should also expand the applications of the XPS and TOF-SIMS techniques.

Recent studies have shown the successful use of a GCIB (gas cluster ion beam) source on XPS (X-ray photoelectron spectroscopy) instruments to quantify the chemical depth profile of polyimide films without sputter induced chemical degradation[1, 2]. Based on these earlier experiments, additional GCIB depth profiling applications of organic and biomaterials with XPS and TOF-SIMS will be discussed. Examples will be presented for the characterization of ultra-thin organic electronic layers in OLED's and OPV's. The successful organic depth profiling to depths of several tens of microns will also be discussed.

1. Takuya Miyayama, Noriaki Sanada, Mineharu Suzuki, John S. Hammond, S. –Q. D. Si and Atsushi Takahara, *J. Vac. Sci. Technol. A*. 2010, A 28(2), L1

2. Takuya Miyayama, Noriaki Sanada, Scott R. Bryan, John S. Hammond and Mineharu Suzuki, *Surf. Interface Anal.* 2010, *42*, 1453–1457.

9:00am **AS-TuM4 Advances in Organic Depth Profiling for Polymer Devices**, ***J.L.S. Lee***, *I.S. Gilmore*, National Physical Laboratory, UK, *A. Licciardello*, University of Catania, Italy

Knowledge of the distribution of organics within an organic matrix is important to the innovation and manufacture of many advanced technologies including polymer electronics and photovoltaics, medical devices, ink-jet printing technologies and drug delivery systems. Organic depth profiling using sputtering with cluster ions and imaging by SIMS or XPS have revolutionised the analytical capability for these important systems, providing uniquely detailed 3D chemical information. However, despite recent progress, organic depth profiling is not yet routinely applied to industry problems. The principal reason for this is that organic sputtering only works for a limited set of materials [1] and unfortunately it fails completely for many industrially important materials, such as conjugated polymers in the organics electronics industry. Consequently, an important recent development is the use of nitric oxide (NO) flooding [2] as a radical scavenger to reduce ion induced cross-linking during depth profiling.

In this study, we use model polymer layers, including polystyrene and industrially relevant conjugated polymers, to demonstrate the benefits of using NO flooding for polymers that do not sputter under normal conditions and evaluate the basic metrology. Understanding the mechanisms for damage, cross-linking, radical generation and radical reaction is vital in developing this technique to work with industrial materials. Using C_{60}^{2+} as a sputtering ion beam, it is found that NO flooding combined with sample cooling [3] significantly reduce the disappearance cross-section for characteristic fragments. For polystyrene model systems, the steady state intensity of $C_7H_7^+$ can be increased from typically < 0.1% of the initial intensity at normal experimental conditions to 50% when NO flooding is used in conjunction with cooling. We also demonstrate successful depth profiles on 1 μm thick polymer material, showing high and constant sputtering yields with ~ 30 nm depth resolution to the interface. Our results show a dramatic improvement for the depth profiling of difficult type II polymers. NO flooding may be used along with other developments e.g. large argon cluster ions [4], sample cooling and sample rotation [3], and has the potential to provide a step change in analytical capability for industrial samples.

[1] C. M. Mahoney. *Mass Spectrom. Rev.*, **2010**, *29*, 247

[2] N. Tuccitto, I. Delfanti, V. Spampinato and A. Licciardello, presented at SIMS XVII, Toronto, **2009**.

[3] P. Sjovall, D. Rading, S. Ray, L. Yang and A. G. Shard, *J. Phys. Chem. B*, **2010**, *114*, 769.

[4] J. L. S. Lee, S. Ninomiya, J. Matsuo, I. S. Gilmore, M. P. Seah and A. G. Shard, *Anal. Chem.* **2010**, *82*, 98.

9:20am **AS-TuM5 TOF-SIMS Depth Profiling and 3D Analysis of Polymer Materials Using C_{60} and Ar Cluster Ion Beams for Sputtering**, ***D. Rading***, ION-TOF GmbH, Germany, *N. Havercroft*, ION-TOF USA, Inc., *R. Moellers, E. Niehuis*, ION-TOF GmbH, Germany

Preservation of molecular information under high-dose sputtering conditions has become increasingly important. It is not only a pre-requisite for depth profiling and 3D analysis of organic materials, but also extends the survival of sample material beyond the static SIMS limit in high lateral resolution imaging. In this respect, the use of a high energy cluster ion beam for sputtering such as SF_5 [1] and C_{60} [2-4] has aroused considerable interest. With the beam energies typically applied, the total energy is high enough for reasonable sputter rates whereas the energy per atom, of about several 100 eV, is considered low enough to minimize sample damage. However, it has been demonstrated that a variety of organic compounds cannot be profiled in a satisfactory way and characteristic molecular secondary ion signals are lost [5-7]. In this respect it has been shown recently that massive argon cluster ions can be successfully applied as primary projectiles in SIMS [8,9].

We equipped a TOF.SIMS 5 instrument with a Bi_n, C_{60} and an Ar_n cluster ion source in order to compare the possibilities and limitations of these projectiles for depth profiling of polymer materials. In this contribution, we will focus on dual beam depth profiling where the analysis is done with Bi_n and the sputtering with C_{60} and Ar_n cluster ion beams, respectively. Stability and intensity of characteristic high mass molecular ion signals as well as sputter yields and depth resolution will be compared. For this purpose different beam energies resulting in 2 - 10 eV/atom for Ar_n and 167 - 667 eV/atom for C_{60} sputtering have been applied to various polymer samples. From our experiments we can conclude that most of the limitations C_{60} sputtering suffers from could be successfully overcome and that the Ar GCIB seems to be a more universal tool for sputtering of organic materials.

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[3] J. Cheng, A. Wucher and N. Winograd, *J. Phys. Chem B.* **2006,** *110,* 8329-8336

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[5] M.S. Wagner, *Anal. Chem.* **2005**, *77,* 911-922

[6] R. Möllers, N. Tuccitto, V. Torrisi, E. Niehuis, A. Licciardello, *Appl. Surf. Sci.* **2006**, *252*, 6509-6512

[7] H.-G. Cramer, T. Grehl, F. Kollmer, R. Moellers, E. Niehuis, D. Rading, *Appl. Surf. Sci*. **2008**, *255,* 966

[8] N. Toyoda, J. Matsuo, T. Aoki, I. Yamada, D.B. Fenner, *Nucl. Instr. and Meth. in Phys. Res.* **2002**, *B 190*, 860-864

[9] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, *Rapid Communications in Mass Spectrometry* **2009**, *23*, 1601-1606

9:40am **AS-TuM6 The zcorrectorgui for 3D ToF-SIMS Depth Profiles**, ***D.J. Graham***, *M. Robinson, D.G. Castner*, University of Washington

ToF-SIMS imaging is a powerful technique for obtaining chemically specific maps of the surface of a wide range of samples including polymers, metals, tissues, and cells. When combined with the sputtering capabilities of modern ToF-SIMS instruments, one can obtain chemically and biologically specific 3D depth profiles, as well as track chemical signatures throughout a sample volume. This is done with a dual beam approach by taking an image of the surface, sputtering away a given amount of the material and then taking a new image of the freshly exposed area. This process is repeated until the object of interest is gone or the desired depth is reached.

When working with surfaces with significant topography such as the surface of a cell, the z axis of the resulting data cube is not correct. This is due to the fact that each image slice of the surface is displayed as a 2-D image taken from a 3-D surface. This results in a type of inverted topography of the 3D structure within the ToF-SIMS image volume. To correct for this, the National ESCA and Surface Analysis Center for Biomedical Problems NESAC/BIO (Seattle, WA) has developed a Matlab (Mathworks, Natick MA) toolbox to correct the z-axis of cell depth profiles and display the data properly.

Since the shape and topography of a cell can be complex, we have created a set of features of known chemistry and controlled geometry in order to test and validate that the zcorrectorgui is accurately correcting the z-axis. For this, microsphere templating was combined with capillary force lithography to create features of known size and shape. The features sizes were chosen to correspond with the sizes of typical eukaryotic cells. Topographical images of these features were obtained by AFM. After AFM analysis the features were depth profiled by ToF-SIMS. The resulting depth profile data was then imported into the zcorrectorgui and processed. In this presentation we will highlight the results from this study and show example data obtained from a real cell depth profile processed with the zcorrectorgui.

10:40am **AS-TuM9 3D Analysis of Organic Multilayer Structures by TOF-SIMS Using Ar Cluster Ions**, ***R. Moellers***, ION-TOF GmbH, Germany, *R. Kersting*, TASCON GmbH, Germany, *D. Rading*, *E. Niehuis*, ION-TOF GmbH, Germany

Organic multilayer systems are of increasing importance in many technological fields. The entry of the OLED technology into commercially available multi-color displays is one example. Optimization of this technology in terms of lifetime and efficiency requires a detailed knowledge of the layer and interface composition.

From the analytical point of view, theses OLED multilayer structures are quite challenging. A detailed analysis requires the identification of complex high mass organic molecules in thin layers of only several nanometer thickness with a lateral resolution in the micrometer range. In particular the identification of the molecular composition is challenging for SIMS as molecular information does usually not survive high dose sputtering conditions.

In the past different projectiles such as low energy Cs^+ [1] and keV C_{60}^+ cluster [2-4] have been explored for their depth profiling capabilities on organic layers. For some materials molecular information survives but for the majority of organic molecules depth profiling using these projectiles fails. Recently the application of large Ar clusters for the non-destructive removal of organic matter has been discussed in the SIMS community. The GCIB (gas cluster ion beam) technique was developed by the group of Isao Yamada [5] at the University of Kyoto and has already demonstrated some potential in this field of application [6].

We used a TOF.SIMS 5 instrument equipped with a Bi cluster ion gun for the analysis and an Ar GCIB as well as an C_{60} cluster ion gun providing both analysis and sputter gun capabilities. In this contribution we will focus on the variation of the sputter projectile, the energy dependence of the resulting depth resolution and the survival of specific molecular ion signal under high dose sputtering conditions. For this purpose a well-defined multilayer model sample similar to a working OLED device was used. The knowledge about the optimum analysis conditions gained on the model system was transferred to a 3D analysis of an OLED display device using an Ar GCIB for sputtering.

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[2] N. Winograd, Anal. Chem. **2005**, April 1, 143A-149A

[3] J. Cheng, A. Wucher and N. Winograd, J. Phys. Chem B. **2006**, 110, 8329-8336

[4] J.S. Fletcher, X.A. Conlan, J.C. Vickerman, N.P. Lockyer, Appl. Surf. Sci. **2006**, 252, 6513-6516

[5] I. Yamada, J. Matsuo, N. Toyoda, A. Kirkpatrick; Materials Science and Engineering: R-Reports. A Review Journal; 34, **2001**, 6, 231-295

[6] S. Ninomiya, K. Ichiki, H. Yamada, Y. Nakata, T. Seki, T. Aoki, J. Matsuo, Rapid Communications in Mass Spectrometry **2009**, 23, 1601-1606

11:00am **AS-TuM10 Molecular Imaging of Cells and Tissues with Novel Ion Beams**, ***J. Matsuo***, QSEC, Kyoto University, CREST, Japan, *K. Ichiki*, *T. Yamanobe*, *Y. Yamamoto*, Kyoto University, Japan, *S. Ibuki*, QSEC, Kyoto University, CREST, Japan, *T. Aoki*, *T. Seki*, Kyoto Univeristy, CREST, Japan

The field of secondary ion mass spectrometry (SIMS) for biological material analysis is receiving much attention nowadays, because molecular, structural and chemical information is considered to be invaluable. However, for large biomolecules the sensitivity of SIMS needs to be improved. Cluster ion beams have been reported to enhance the yields of secondary ions, because of the high-density energy deposition and multiple collisions near surfaces. SF_5, C_{60}, Au_3 and Bi_3 were found to be quite useful for SIMS of organic materials.

We have proposed using a large Ar cluster beam for organic SIMS. This beam has a number of advantages over other cluster beams for molecular depth profiling of various polymers, and it provides new opportunities for sputtering molecules without inducing significant damage [1]. Biomolecules are also very fragile and thus difficult to sputter with conventional ion beams; therefore, a large Ar cluster beam would be quite suitable for biological material analysis. However, molecular imaging requires a focused Ar cluster beam, and we developed a new Ar cluster ion gun aiming to obtain a fine-focused beam of several mm diameter. An orthogonal acceleration time-of-flight (oa-TOF) mass spectrometer, which allows the use of a continuous beam, was also combined in the system, and a mass resolution higher than 6000 was obtained. Because there was no need to use the ion-bunching technique in this system, there was no tradeoff between beam diameter and mass resolution. This is another advantage of this molecular imaging system over the conventional TOF instrument. This novel system is quite useful for both molecular depth profiling and imaging.

The latest results of this system and its performance in molecular imaging of cells and tissues will be presented and discussed.

[1] J. Matsuo, S. Ninomiya, H. Yamada, K. Ichiki, Y. Wakamatsu, M. Hada, T. Seki and T. Aoki, Surf. Interface Anal. (2011) 42, 1612

11:20am **AS-TuM11 High Resolution TOF-SIMS Imaging of Barrier Layers in Mouse Skin Stratum Corneum**, *I. Ishizaki*, ULVAC-PHI inc., Japan, *A. Kubo*, Keio University, Japan, *Y. Ohashi*, *A. Yamamoto*, ULVAC Inc., Japan, *J.S. Hammond*, *G.L. Fisher*, ***S.R. Bryan***, Physical Electronics

The stratum corneum (SC) is the outermost layer of epidermis that acts as a barrier to keep foreign objects out of the body and to keep water in. It is composed of multi-layered sheets of dead cells containing keratin that continuously fall off and are regenerated from live cells in the underlying layers. The total thickness of the SC layer is less that 40 µm. In order to study the barrier properties of the SC and how this function fails in certain skin disorders, it is necessary to visualize the distribution of different biomolecules within the multi-layered SC structure. It is also valuable to compare the penetration of various foreign chemicals into the SC layer in mice with and without the skin disorder. In this initial study, we applied TOF-SIMS imaging using a bismuth cluster ion beam to characterize the multi-layer structure of mouse skin. Samples were prepared by quick freezing of mouse tails followed by cross-sectioning by cryostat. TOF-SIMS imaging provided the spatial resolution and molecular specificity to clearly visualize dead cell layers and living layers of the epidermis. By using peaks characteristic of specific molecules, it was possible to image the distribution of amino acids, cholesterol, and lipids within the SC. The results suggest that SC might contain several chemically distinct layers. Skin samples were also depth profiled using GCIB sputtering. Imaging of cross-sections and depth profiling from the skin surface will be compared for obtaining molecular profiles within the SC structure.

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