Applied Surface Science
Room: Cochiti - Session AS-WeA

Surface Mass Spectrometry: SIMS and Beyond
Moderator: C. Szakal, National Institute of Standards and Technology

2:00pm **AS-WeA1 Exploring the Surface Sensitivity of ToF-SIMS: Measuring the Implantation Depths and Sampling Depths of Bi_n and C_{60} Ion Sources in Organic Films**, ***S. Muramoto***, *J. Brison, D.G. Castner*, University of Washington

When a pulsed Bi_n^+ analysis beam and a direct current C_{60} etching beam are used in ToF-SIMS dual-beam depth profiling, we observed that increasing the ion dose of the analysis beam decreased the molecular signal as a function of depth. This decay was seen to occur much earlier in the depth profile for less clustered ions, suggesting that damage is related to the implantation depth of the primary ion. Recent experimental and simulation results in this field indicate that implantation depth is inversely related to the clustering of the primary ion, and are observed to affect outcomes such as sputter yield and escape depth (sampling depth). There is a need to characterize these parameters on organic systems, since a better understanding of these parameters will help us choose experimental parameters for the optimal analysis of samples.

In this study, the above mentioned quantities for Bi_n^{q+} (n = 1, 3, 5, q = 1, 2) and C_{60}^{++} ions were characterized on molecular and polymeric organic films; a spin-cast trehalose and a plasma polymerized tetraglyme, both about 100 nm thick. The implantation depths of Bi ions were determined using C_{60} single-beam depth profiling of the same area bombarded by bismuth. The depth scale was calibrated using AFM. The sputter yield was obtained by AFM imaging of the sputter crater. The molecular escape depth was determined by capping a protein-adsorbed mica with tetraglyme overlayers of varying thicknesses and monitoring the protein fragment intensities as a function of thickness. Results show that an ion's penetration depth is directly proportional to the energy-per-constituent of the ion. For example, increasing the number of Bi atoms from 1 to 3 (Bi_1^+ to Bi_3^+) for 25 keV single charged ions decreased the average penetration depth from 18 to 10 nm. When the energy of Bi_3 was increased from 25 to 50 keV, the implantation depth increased from 10 to 14 nm. When implanting bismuth ions, we observed etching of the sample surface, with the crater depths proportional to the cluster size of the bismuth ion. These crater depths were also proportional to the escape depth of the protein fragments. Bi_1^+ at 25 keV was found to be the most surface sensitive; its sampling depth was only 1.8 nm despite its implantation of 18 nm. The second most surface sensitive was C_{60}^{++} at 20 keV with a molecular escape depth of 2.4 nm. It turned out that the single most important factor that determined the surface sensitivity of the ion source was its sputter depth; both Bi_1^+ and C_{60}^{++} eroded 0.3 and 1.0 nm, respectively, whereas Bi_5^{++} with a sputter depth of 1.8 nm was the least surface sensitive with a molecular escape depth of 4.7 nm.

2:20pm **AS-WeA2 A New Cluster Ion Beam for Advanced Molecular Depth Profiling of Polymers by TOF-SIMS**, *T. Miyayama, S. Iida, N. Sanada, M. Suzuki,* ULVAC-PHI, Japan, *G.L. Fisher, J.S. Hammond,* ***S.R. Bryan***, Physical Electronics

The introduction of C_{60}^+ as a sputter beam for TOF-SIMS made it possible to acquire molecular depth profiles on a wide variety of polymers. Previous studies by many different groups have demonstrated that not all polymers can be successfully depth profiled and that certain classes of polymers undergo sputter-induced chemical reduction when bombarded by C_{60}^+ ions. If the polymer sputter yield is not high enough, the subsurface sputter-induced damage will accumulate as a function of sputter ion dose and the secondary molecular ion signals will not be stable. A number of different analytical parameters have been previously explored in attempts to improve depth profiling of these difficult polymers including sample temperature, beam energy, and incidence angle. We reported last year that glancing C_{60}^+ incidence angle (76° from surface normal) significantly improved the ability to depth profile polycarbonate and polystyrene, which were previously unsuccessful at a typical incidence angle of 48°. However, even under these optimized conditions, the depth profiles eventually fail after several hundred nanometers due to accumulated sputter damage to the polymer and a concurrent reduction of the secondary ion and sputter yields. In the present study, we report the efficacy of an argon gas cluster ion beam (GCIB) for steady-state molecular depth profiling the same polymer systems. Depth profiles using different GCIB experimental conditions will be reported and compared to C_{60}^+ depth profiles acquired under optimized conditions.

2:40pm **AS-WeA3 Nanoparticle Surface Analysis by Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Low Energy Ion Scattering (LEIS)**, ***T. Grehl***, *P. Bruener, E. Niehuis,* ION-TOF GmbH, Germany, *N. Havercroft,* ION-TOF USA, Inc., *R. ter Veen, M. Fartmann, D. Breitenstein*, Tascon GmbH, Germany

Due to their extraordinary properties nanoparticles enter more and more fields of industrial production and daily life. They facilitate the protecting effect of sun creams, make car coatings and spectacle lenses scratch resistant and reliably protect shoes from wetness. Nanoparticles with antibacterial properties are used in clothing and refrigerators.

Nanoparticles' properties are influenced by their high surface to volume ratio. In addition, specifically tailored nanoparticles are increasingly composed of core shell structures. In order to understand and further develop the properties of nanoparticles it is therefore important to develop tools to investigate the elemental and molecular composition of their surfaces and interfaces.

Two ion beam technologies show promising features in this respect: On the one hand Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is able to probe the outermost 3-5 atomic layers of a sample. It reveals the elemental as well as the molecular composition of the samples' surface in a semi-quantitative manner. On the other hand, Low Energy Ion Scattering (LEIS) is a quantitative technique to probe the elemental composition of the outermost atomic layer. Combining these two complementary techniques allows a comprehensive overview on the sample composition.

In our study we will present combined ToF-SIMS and LEIS data on model-nanoparticle systems and will give examples for their prospects to enable nanoparticle development, product control and failure analysis. Amongst others, the layer growth of a shell of Al_2O_3 on $LiMn_2O_4$ nanoparticles deposited by an ALD process was investigated. Both techniques are able to determine the increased coverage of the core. While ToF-SIMS yields additional information about organic residues, LEIS is able to quantify the surface composition and assess the integrity of the layer.

3:00pm **AS-WeA4 Dual Beam Depth Profiling of Organic Materials by Time-of-Flight Secondary Ion Mass Spectrometry under Optimized Ion Beam Conditions**, *D. Rading, R. Moellers, F. Kollmer, T. Grehl,* ION-TOF GmbH, Germany, ***N. Havercroft***, ION-TOF USA, Inc., *E. Niehuis*, ION-TOF GmbH, Germany

In recent years the development of sputter depth profiling of organic materials using Time of Flight instruments has made rapid progress. In particular, the use of a high energy C60 cluster ion beam for sputtering has drawn considerable interest [1-3]. However, it has also been demonstrated that a variety of organic compounds cannot be profiled in a satisfactory way as characteristic molecular secondary ion signals are lost under high dose cluster ion bombardment [4-6]. In a number of studies various approaches were applied in order to overcome this problem. These approaches included sputtering at low incident angles [7], sputtering with low energy Cs ions [8], cooling or heating of the sample [5,9,10] and using alternative cluster ion sources such as massive argon clusters [11]. As a suitable sample for more detailed studies on properties, such as depth resolution was not available, most of the work so far was of phenomenological kind, i.e. it was checked whether characteristic organic signals survived the sputter process.

In this contribution, we investigate the influence of sputtering and analysis beam conditions on the signal intensity of characteristic high-mass molecular ions under high primary ion flux. For this purpose a series of primary ion species (C60, Bin, Cs) at various energies and angles has been applied. In a second step an Irganox multilayer sample introduced by NPL [10] was used to investigate the influence of energy and angle of a C60 sputter beam as well as the influence of sample rotation on depth resolution, constancy of the sputter rate and quantification possibilities in organic depth profiling.

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4:00pm **AS-WeA7 Fundamental Sputtering Yields of Nanoparticles using SIMS***, **J.L.S. Lee**, I.S. Gilmore, D.C. Cox, M.P. Seah, S.J. Spencer*, National Physical Laboratory, UK

Nanoparticles are front-runner nanotechnologies key to high innovation products, such as biodiagnostics, drug delivery, medical imaging (contrast agents), cosmetics, sunscreens and catalysts. The surface and bulk chemistries of nanoparticles are crucial for their unique properties. There is also increasing concern over the potential health, environmental and safety risks of nanomaterials. Robust and consistent methodologies for characterising nanoparticle surface and bulk chemistries are urgently needed to support standardisation, regulatory requirements and toxicology studies [1].

Secondary ion mass spectrometry (SIMS) has been applied in nanoparticle characterisation [2,3]. However, the fundamentals of the sputtering of nanoparticles are not yet well understood. The sputtering yield is expected to be significantly different for nanoparticles compared to bulk materials, due to the dimension of nanoparticles being similar to the size of the SIMS collision cascade, and the larger available surface area for secondary emission. In this study, SIMS depth profiles were obtained for model Au nanoparticles, with diameters ranging from 10 nm – 100 nm, dispersed and mounted onto a silanised silicon substrate. The sputtering yields and profile shapes are evaluated for both atomic and cluster primary ion beams (Ar^+, Bi^+, Bi_3^+ and $C_{60}{}^{n+}$), using a range of primary ion energies. The nanoparticles are characterised by SEM and AFM both before and after sputtering. There is a significant increase in the sputtering yield for nanoparticles compared with bulk materials, in agreement with predictions from a recent molecular dynamics study [4]. In addition, for the first time, we observed the sputtering of nanoparticles in real time using a focused ion beam system with simultaneous SEM imaging. This provides valuable information for interpreting the SIMS depth profiles of nanoparticles and an interesting phenomenon of nanoparticle coalescence was observed. These results contribute towards developing the essential underpinning metrology and providing a practical procedure to analysts for the chemical characterisation and compositional depth profiling of nanoparticles.

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4:20pm **AS-WeA8 SIMS: Cluster Primary Ion Sputtering - Practical Reference Data and Outlook for High-Resolution Organic Imaging***, **I.S. Gilmore**, T.L. Salter, J.L.S. Lee, F.M. Green, M.P. Seah*, National Physical Laboratory, UK

Cluster ions have become the ion beam of choice for the analysis of organics in ToF-SIMS, owing to the large enhancement of the molecular ion yield [1] and the ability to depth profile through certain organic materials [2,3]. However, there is currently a lack of practical reference data on the sputtering yield volumes and damage cross-sections for commonly encountered materials in industry. Aside from having fundamental importance, these data can aid analysis by informing optimal analysis parameters, such as the useful lateral resolution achievable [4]. In this work, a systematic study using Bi+, Bi3+, Bi5+ and C60+ ions is conducted for industrially relevant organics (PMMA, PVP, hydroxypropyl cellulose, phenylalanine, cholesterol, rhodamine and Irganox 1010). We provide general recommendations to help analysts.

For some organic materials thicker than a monolayer, the traditional static SIMS limit may be exceeded since the secondary ion intensity is retained as the material is consumed. The useful lateral resolution may therefore be improved by integrating intensity. However, the ultimate lateral resolution is also limited by the ion source brightness. The reference data here and ion source design constraints define the present frontier of SIMS in terms of spatial resolution and molecular information. We show how this frontier has moved forward dramatically over the last 10 years and what barriers need to be overcome to allow nanoscale molecular imaging in SIMS.

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4:40pm **AS-WeA9 Sample Preparation of Cellular Samples for ToF-SIMS Analysis***, **M.A. Robinson**, D.G. Castner*, University of Washington

Over the last decade time-of-flight secondary ion mass spectrometry (ToF-SIMS) has been increasingly used for examining (imaging) biological samples ranging from surface immobilized proteins to tissue sections to single cells. Due to the ultra high vacuum requirement of the ToF-SIMS technique careful and stringent sample preparation protocols are necessary to preserve the native state of these samples. There are a variety of preparation procedures that have been developed to address this need. However, there is still debate as to which procedure best preserves cell chemistry and morphology. The goal of this study is to further elucidate the differences in information that can be obtained when comparing cellular samples that have been plunge cooled and then freeze dried versus those that have been plunge cooled and analyzed in the frozen hydrated state.

Freeze drying biological samples after cryofixation is a much simpler method of sample preparation compared to frozen hydrated. We have shown that freeze drying cryofixed samples preserves the native morphology as well as the K^+/Na^+ gradient in single NIH 3T3 fibroblasts, as shown in Figures 1a and 1b. Given optimal preparation procedures, images of subcellular compartments can be realized, as seen in Figure 1c. A single cell is shown after $C_{60}{}^{++}$ sputtering ($C_{60}{}^{++}$ ion dose = 4.3×10^{14} ions/cm^2). The nucleus can be seen in the circular area within the cell that lacks $C_3H_8N^+$ signal. A nucleolus is observed as the bright spot within the nucleus. Also noticeable is the $C_3H_8N^+$ signal is the Golgi apparatus in the perinuclear region.

The question that remains is what type of information can be obtained from samples that have been freeze dried? Some groups have reported that freeze drying will cause cellular damage [1], while others have reported detrimental effects from frozen hydrated analysis [2]. Freeze drying continues to be the most popular preparation method after cryofixation, most likely because it is less complex than frozen hydrated analysis, as well as the fact that few ToF-SIMS instruments are setup to easily perform this type of investigation. We are adapting a liquid nitrogen cooled sample stage to allow for the rapid entry of cellular samples at liquid nitrogen temperatures to avoid sample warming and ice crystal formation. Ice crystal formation must be avoided in frozen hydrated analysis of biological material, as ice crystal formation will rupture cell membranes causing a loss of morphological and chemical information.

The results from this study shows the differences in information obtained when analyzing similar cellular samples in the freeze dried state versus the frozen hydrated state.

5:00pm **AS-WeA10 "Wet SIMS": A Novel Molecular Imaging Technique for Biological Material Analysis***, **J. Matsuo**,* Kyoto University, CREST, Japan*, H. Yamada, Y. Wakamatsu,* Kyoto University, Japan*, T. Aoki, T. Seki*, Kyoto University, CREST, Japan

Because of the complexity of the structure and chemical composition in living organisms, much progress has been made in realizing mass imaging for biological samples. Secondary ion mass spectrometry (SIMS) imaging technique has the significant advantage of high spatial resolution, free of matrix deposition and with good reproducibility. In conventional SIMS the primary probes are keV-energy ion beams, which deposit their energy to atomic nuclei. As a result, primary ions break molecular bonding, and molecular information is lost. On the other hand, MeV-energy ions enhance ionization of high mass molecules, because of their dense electronic excitation. Molecular images with lateral resolution of around 5 mm have been demonstrated for peptides or lipids using MeV-energy ion beams [1].

In addition, MeV-energy ions, which have a long projection range in matter, can be utilized for material analysis under low vacuum. The low-vacuum condition prevents evaporation of water from the biological sample and helps maintain the shape of the sample. A new instrument has been developed to realize SIMS measurements under low vacuum. Biological samples were analyzed with swift heavy ions, and secondary molecular ions

were introduced into a quadrupole ion guide combined with a differential pumping system. An orthogonal time-of-flight (o-ToF) retaining high vacuum was employed to measure secondary ion mass spectra. This system allows the use of continuous beam, because of collisional cooling and orthogonal extraction. The mass resolution of this system is better than 6000, and is independent on the primary beam. Molecular imaging of cells and tissues was observed with a sample-scanning system. Secondary emitted biomolecular ions, such as lipids or cholesterols, were clearly observed with sufficiently high intensity. This new technique opens new possibilities for SIMS analysis, and we called it "wet SIMS".

Recent progress in this novel technique will be presented and discussed in view of its possible application in the analysis of biological matter.

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5:20pm **AS-WeA11 Improvement of Organic Ion Yields in Secondary Ion Mass Spectrometry via Water Vapor Injection***, **T. Mouhib**, A. Delcorte, C. Poleunis, P. Bertrand*, Université Catholique de Louvain, Belgium

Even though significant progress has been achieved in molecular characterization by secondary ion mass spectrometry (SIMS) of organic compounds, some challenges still exist. One important limitation concerns the sensitivity the technique, often insufficient for high resolution molecular imaging. Several approaches have been proposed to increase the useful molecular signal intensities. The first one involves specific sample preparation procedures, such as the use of special matrices or metal-assisted SIMS (MetA-SIMS), in which metal nanoparticles are condensed on the sample surface. The second type of improvement directly involves the choice of the projectile, i.e. atomic projectiles are replaced by clusters, such as Au_n^+, Bi_n^+, C_{60}^+ and SF_5^+.

In this contribution, we investigate a new protocol to improve the analytical performance in organic SIMS, using water vapor injection at relatively high pressure near the sample surface. A significant enhancement of the positive secondary ion intensities is observed for organic materials irradiated with 12 keV Ga^+ ions in the presence of H_2O gas. In addition, our results show that the enhancement depends on the type of secondary ion and that the formation of protonated ions is specifically favored. For the low molecular weight additive Irgafos 168 ($C_{42}H_{63}O_3P$), the normalized $[M+H]^+$ intensity increases by more than 50 times upon H_2O flooding. The enhancement factors are lower with high molecular weight polymers. Nevertheless, the intensity of the protonated monomer ions is also enhanced preferentially in comparison with those of the deprotonated and the bare monomer ions. In the next phase of this work, we consider the combination of H_2O vapor flooding with polyatomic projectile bombardment.

5:40pm **AS-WeA12 IonCCD^{TM} for Charged Particle Detection: From sub-keV Electrons and keV Atomic and Molecular Ions to Hyperthermal Biomolecular Ions***, **O. Hadjar***, OI Analytical*, W.C. Schnute,* Dionex Corporation*, J. Laskin*, Pacific Northwest National Laboratory

We will present the latest data using a pixel array for charged-particle detection based on a modified charge-coupled device technology (IonCCD^{TM}). The array is 51 mm long, consists of 2126 pixels (1.5 mm long) with 0.024 mm pitch. The charged particle beam is collected individually by each pixel, and hence, the IonCCD signal response is proportional to the beam flux and the collection time (integration time). With an integration time of 82 µs and a readout time of 2.7 ms, the IonCCD produces 360 frames a second. We will present data showing the direct use of the IonCCD as a beam profiler (one dimensional) to characterize the positively and negatively charged ion beams exiting an RF-only collisional quadrupole. The latter is used to thermalize and collimate the ions produced by an atmospheric pressure electrospray source. When mounted on the focal plane of a miniature Mattauch-Herzog geometry sector-field analyzer, the IonCCD produces a mass-over-charge (m/z) spectrum of the produced ions. For high sensitivity measurements we coupled the IonCCD to a micro-channel plate (MCP). In this manner, the IonCCD is used as an anode to read the electrons produced by the MCP. We will present MCP-IonCCD mass spectra using an electron-impact (EI) source to produce singly and doubly charged Xe ions. We compare the performance of the MCP-IonCCD hybrid detector to that of the IonCCD itself. We will apply this technology to the simultaneous m/z separation and detection of negative ions produced by electrospray ionization that generates beams of deprotonated molecules that are typically 10 times weaker than ion beams produced in the positive mode.

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