

# Wednesday Afternoon, October 22, 2008

## Applied Surface Science

Room: 207 - Session AS-WeA

## Frontiers of Analysis and Combined Materials

**Moderator:** D.J. Gaspar, Pacific Northwest National Laboratory

1:40pm **AS-WeA1 Ambient Surface Mass Spectrometry – DESI – Towards a Metrological Framework**, *F.M. Green*, National Physical Laboratory, UK, *P. Stokes*, *G. O'Connor*, LGC Ltd., UK, *I.S. Gilmore*, National Physical Laboratory, UK **INVITED**

There has been an explosion in the growth of ambient surface mass spectrometries with new ionisation and desorption methods developing rapidly. Surface chemical analytical techniques such as SIMS are extremely powerful providing high-sensitivity molecular information at better than 200 nm spatial resolution. However, the requirement for analysis in vacuo is for many applications a severe drawback. This is, of course, particularly important in biology. In the vanguard of these ambient methods is Desorption Electrospray Surface Ionisation (DESI) developed by the Cooks group.<sup>1,2</sup> DESI has already been shown to have great potential in a wide range of application areas from forensics and homeland security, through to counterfeit detection of pharmaceuticals and biological analysis. Of the wide variety of desorption methods it is clear that DESI has one of the strongest uptakes and so it is with DESI that we begin the development of a metrological approach, similar to that developed for SIMS and XPS. The objective is to improve repeatability and reproducibility and consequently confidence in the method and uptake into industry. A first step in the development of a metrological framework is to measure and improve repeatability. Here we conduct a systematic study of the parameters affecting spectral intensities and the interaction of the electrospray jet with the material surface. We have developed a well-controlled model system of Rhodamine B on glass that allows the effect of key experimental parameters such as geometry and spray conditions to be studied and optimised. Using this approach we have improved the repeatability of spectral intensities to 20%. In addition, we have studied the surface crater and surrounding disrupted material which gives insights into the interaction mechanism of the electrospray jet and the surface. This is important to allow future improvements in resolution and to understand the rate at which material is removed.

<sup>1</sup> Z. Takats, J. Wiseman, B. Gologan, G. Cooks; *Science*, 306 (2004) 471

<sup>2</sup> G. Cooks, Z. Ouyang, Z. Takats, J. Wiseman, *Science*, 311 (2006) 1566.

2:20pm **AS-WeA3 Shallow-Depth Surface Etching by Electrospray Droplet Impact**, *K. Hiraoka*, *Y. Sakai*, *D. Asakawa*, University of Yamanashi, Japan, *Y. Iijima*, JEOL Ltd.

A new ionization method, electrospray droplet impact (EDI) ionization, has been developed for matrix-free secondary ion mass spectrometry (SIMS).<sup>1,2</sup> The charged water droplets formed by electrospraying 1M acetic acid aqueous solution at atmospheric pressure are sampled through an orifice with a diameter of 400  $\mu\text{m}$  into the first vacuum chamber, transported into a quadrupole ion guide, and accelerated by 10kV after exiting the ion guide. The water droplets impact on a dry solid sample (no matrix used) deposited on a stainless steel substrate. The secondary ions formed by the impact are transported to a second quadrupole ion guide and mass-analyzed by an orthogonal time-of-flight mass spectrometer (TOF-MS). EDI was applied to peptides, synthetic polymers, and inorganic materials. It was found that EDI/SIMS has a high sensitivity without damaging the sample underneath and the film thickness desorbed by a single collisional event is to be less than a few monolayers. An instant conversion (in subpicoseconds) of kinetic energy of the impinging water droplet to the internal energies of molecules in the colliding seldedge takes place, i.e., sample molecules in the shock-wave excited seldedge suffer from the electronic excitation leading to the desorption/ionization. In the EDI mass spectra for PET, several fragment ions were observed but the XPS spectra did not change with prolonged cluster irradiation. This indicates that the surface of PET was etched with little surface damage. In the EDI mass spectra for tin and silicon, the major secondary ions observed were protonated oxide ions such as  $\text{H}^+(\text{SnO})_n$  and  $\text{H}^+(\text{SiO}_2)_n$ . This suggests that the oxidative chemical etching takes place in the seldedge of the colliding interface resulting in the atomic-level surface etching. Acknowledgement: This work was supported by the Japan Science and Technology Agency

<sup>1</sup> K. Hiraoka, D. Asakawa, S. Fujimaki, A. Takamizawa, K. Mori, *Eur. Phys. J. D* 38 (2006) 225.

<sup>2</sup> K. Hiraoka, K. Mori, D. Asakawa, *J. Mass Spectrom.*, 41 (2006) 894.

2:40pm **AS-WeA4 Application of TOF-SIMS and LEIS for the Characterization of Ultra-Thin Films**, *T. Grehl*, *D. Rading*, *E. Niehuis*, ION-TOF GmbH, Germany, *R. ter Veen*, *H. Brongersma*, Calipso BV, The Netherlands, *M. Fartmann*, *B. Hagenhoff*, TASCAN GmbH, Germany

The continuous scaling of semiconductor devices (film thickness, junction depth) to smaller dimensions increases the challenges for the established analytical methods. In addition, new and more complex materials are introduced into the devices. Secondary Ion Mass Spectrometry (SIMS) and more recently Time-of-Flight (TOF-) SIMS have become workhorses for the semiconductor industry. The depth distribution of implants as well as impurities is regularly monitored using Cs and  $\text{O}_2$  sputter depth profiles. Meanwhile sputter energies as low as 200 eV are routinely used in order to achieve a high depth resolution. Even at these low sputter energies the transient effects prevent establishing a reliable depth scale and deriving quantitative information on the first few nm. In addition, concentrations exceed the dilute limit, thus further complicating the quantification process. In this situation, complementary techniques become increasingly important. One of the emerging techniques is Low Energy Ion Scattering (LEIS) using high sensitivity analyzers. It is extremely surface sensitive and provides quantitative information on the outermost atomic layer of a solid. Low energy (1 – 10 keV) noble gas ions (He, Ne, ...) are used as projectiles. The energy of the back-scattered ions from elastic collisions is characteristic for the masses of the target atoms and is measured using an electrostatic energy analyzer. Quantification is comparatively straightforward and bulk standards can be used to determine the sensitivity factors. In addition, information can be gained on the surface near depth distribution of elements (1 – 10 nm) by measuring the extra energy loss of ions scattered in deeper layers (non destructive, "static mode"). This can be combined with conventional sputter depth profiling using a separate beam of low energy noble gas ions ("dynamic mode").

In order to compare the performance of LEIS with TOF-SIMS results for the characterization of ultra-shallow layers we studied a variety of typical sample systems such as ultra-shallow As implants, high-k films, and diffusion barriers at different stages of ALD growth. The results are discussed with respect to information depth, ease of quantification and sensitivity. It can be shown that the static profiling approach of LEIS is extremely powerful in the first few nm of the profile whereas due to its higher sensitivity SIMS performs better after sputtering through the transient region.

3:00pm **AS-WeA5 Use of Ion-Solid Interaction Theory to Optimize FIB Processes**, *L.A. Giannuzzi*, FEI Company

Focused ion beam (FIB) techniques have been used over the years to prepare specimens for characterization in a wide range of analytical instruments. One of the more popular uses of FIB is for the production of transmission electron microscopy (TEM) specimens. The advent of FIB for the preparation of specimens for 3D atom probe tomography (APT) allows for analysis of multi-phased and multi-layered materials which in the past would have been considered difficult or impossible due to specimen preparation constraints. In addition, FIB prepared surfaces are now routinely used for the acquisition of electron backscatter diffraction (EBSD) patterns. This technique has been extended to the acquisition of 3D crystallography in a DualBeam (FIB+SEM) instrument. Typical FIB instruments operating at 30 keV can result in sufficient lateral ion implantation and/or amorphization surface damage to hinder quantitative high resolution TEM results. Amorphization damage can also degrade the quality of the EBSD pattern such that the pattern cannot be resolved. In addition, 30 keV FIB milling can cause sufficient ion mixing which can destroy the chemical/elemental integrity of interfaces, rendering the 3D APT analysis useless. New advances in ion columns allow for imaging and FIB milling to take place down to 500 eV. Specimens can be prepared using the fine probe size of the high energy beam, and then polished with low energy ions which replace the high energy implantation damage with minimal damage from the lower energy ions. These low energy FIB techniques allow for quantitative high resolution (S)TEM, improve the quality of the EBSD patterns, and allow for 3D APT without interferences from the  $\text{Ga}^+$  ion implantation. In addition, since materials exhibit different collision cascade characteristics as a function of incidence angle, prototyping can be optimized by controlling the incidence angle and scan direction of the ion beam which can influence the profile and aspect ratio of the milled region.

4:00pm **AS-WeA8 C60 Bombardment of Si - New Insights from SIMS and TEM**, *G. Gillen, C. Szakal, A. Herzing, I. Anderson*, National Institute of Standards and Technology, *S. Hues*, Micron Technology, *J. Bennett*, Process Characterization Laboratories, ATDF

There is continued interest in the development of novel cluster primary ion beams for applications in Secondary Ion Mass Spectrometry (SIMS). A C60 primary ion incident on a silicon substrate with an impact energy of 3000 eV would dissociate into 60 carbon atoms, each with an impact energy of only 50 eV. Since the depth resolution of a SIMS depth profile is directly related to the primary projectile energy, the use of such a cluster ion provides a possible method for obtaining ultra-high resolution SIMS depth profiles. Based on our previous experience with depth profiling of semiconductor materials using smaller cluster beams, it was hoped that C60 cluster SIMS would provide large improvements in depth resolution over conventional SIMS. Unexpectedly, initial evaluation of C60 SIMS depth profiling using delta-doped test samples demonstrated that deposition of an amorphous carbon layer on the silicon substrate was common, limiting the utility of C60 for depth profiling at impact energies below ~12 keV. Higher bombardment energies can minimize deposition but substantial degradation in depth resolution is observed compared to conventional SIMS depth profiling. This degradation was initially thought to result only from the formation of surface topography. In this work we have investigated the nature of the altered layer produced by C60 bombardment of silicon using SIMS and cross sectional transmission electron microscopy (TEM). Surprisingly, TEM imaging suggests the depth of penetration of carbon into the silicon substrate is substantially greater than would be predicted by simple ion implantation models. Furthermore, the buried interface between crystalline silicon and the carbon-rich altered layer exhibits nm scale roughness. These observations may help to explain the degradation in depth resolution commonly observed in C60 depth profiling of silicon materials. The enhanced diffusion of carbon beyond the penetration depth of the C60 may be explained by the enhanced diffusion of carbon in silicon resulting from strain produced in the silicon by high dose carbon implantation.

4:20pm **AS-WeA9 Understanding the Relationship between Chemical Vapor Deposition Precursor Structure and Film Properties by Application of Electron, Optical, Ion, and X-ray Characterization Methods**, *B.W. Schmidt, B.R. Rogers, R.D. Geil*, Vanderbilt University

Ceramic oxides such as  $\text{Al}_2\text{O}_3$  and  $\text{HfO}_2$  are desirable in microelectronics as high- $\kappa$  replacements of  $\text{SiO}_2$  and in high temperature applications as protectants. For multi-component systems like CMOS devices and thermal barrier coatings, characterization and control of bulk and interfacial properties are important for optimal performance. Chemical vapor deposition (CVD) is popular for its high deposition rates and good conformality. However, final properties of a CVD film can be greatly influenced by the choice of precursor. Novel precursor ligand designs are used to increase volatility and precursor throughput, but can also affect film composition, microstructure, and the deposition window. In this study, ligand effects are investigated by understanding the deposition processes of dimethylaluminum isopropoxide (DMAI) and methylaluminum diisopropoxide (MADI). These are derivatives of popular precursors trimethylaluminum (TMA) and aluminum triisopropoxide (AIP). TMA is well-suited for CVD bubbler delivery systems due to its high vapor pressure and liquid state at room temperature, but is dangerous to handle and requires an oxidant source. AIP has the advantage of being a single-source precursor for  $\text{Al}_2\text{O}_3$ , but requires melting at 130°C to achieve consistent precursor flux. DMAI and MADI represent one and two methylisopropoxide substitutions of TMA, respectively. A goal is to achieve a single precursor with beneficial characteristics of TMA and AIP. Film characterization by X-ray photoelectron spectroscopy (XPS), Auger electron spectroscopy (AES), spectroscopic ellipsometry, and medium energy backscattering spectrometry provide insight into initial stage and bulk deposition. Correlation of composition, microstructure, and chemical state progression to deposition conditions will aid in the development of application-specific precursors.

4:40pm **AS-WeA10 The Interface Formation between Calcium and Poly(3-hexylthiophene) Investigated with Adsorption Microcalorimetry, High-Resolution XPS and ISS**, *F. Bebensee*, Universitaet Erlangen, Germany, *J.F. Zhu*, University of Science and Technology of China, *J.H. Baricuatro, J.A. Farmer, W. Lew*, University of Washington, *H.-P. Steinrueck, J.M. Gottfried*, Universitaet Erlangen, Germany, *C.T. Campbell*, University of Washington

Regioregular poly(3-hexylthiophene) (rr-P3HT), a semiconducting polymer, is widely used in organic electronics (OLED, OFET). Both the interface structure and the interaction strength between the polymer and the electrode (e.g. Ca) are very important for the performance of such devices. The heat of adsorption, which directly reflects the bonding energy between the metal and the polymer, was probed using adsorption microcalorimetry. We find high initial heats of adsorption indicating a strong interaction between Ca

and rr-P3HT. In high-resolution X-ray photoelectron spectroscopy (XPS) experiments, a substantial shift of the S 2p signal suggests electron transfer from Ca to S in the polymer. We therefore conclude that the high initial heat of adsorption is due to the interaction of Ca atoms with S in the sample. Furthermore, shifts of the C 1s signal imply a band bending of about 0.5 eV, while no hints for structural degradation of the polymer can be found. Ion scattering spectroscopy (ISS) measurements suggests that the initial Ca reacts below the surface, followed by 3D Ca island growth. Both of these observations are corroborated by the XPS measurements. We also investigated the effects of electron irradiation of the polymer surface prior to Ca evaporation. Financial support by the DAAD and the NSF is gratefully acknowledged.

5:00pm **AS-WeA11 Synthesis and Characterization of Core/Shell Nanoparticle Thin Films for Gas Analytical Microdevices**, *M. Bruns, M. Fuchs, R. Ochs, S. Schlabach, D.V. Szabó*, Forschungszentrum Karlsruhe GmbH, Germany, *T. Grehl, S. Kayser*, ION-TOF GmbH, Germany, *M. Fartmann*, Tascon GmbH, Germany

Sputtered  $\text{SnO}_2$  thin films are well established as gas sensing layers in analytical micro systems such as the Karlsruhe micro nose (KAMINA). To improve the performance towards higher sensitivity a very promising approach is to replace the sputtered thin films with films made of  $\text{SnO}_2$  nanoparticles. This can easily be achieved by the Karlsruhe microwave plasma process (KMPP), a versatile precursor based gas-phase plasma process suited to synthesize nanoscaled particles with diameters less than 5 nm.<sup>1</sup> Regarding long-term stability, such  $\text{SnO}_2$  nanoparticles can be coated in-situ with a protective ultra-thin  $\text{SiO}_2$  shell in a downstream step and then directly deposited onto the respective micro devices. These core/shell nanoparticles are expected to prevent the gas sensitive core from growing and agglomeration, respectively, while preserving electrical contact. The prerequisite is to achieve an inhomogeneous  $\text{SiO}_2$  shell enabling direct contact between adjacent  $\text{SnO}_2$  nanoparticles, i.e. simply acting as a spacer.

This contribution focuses on the characterization of nanoparticle thin films with a thickness of 200 nm made of core/shell  $\text{SnO}_2/\text{SiO}_2$  nanoparticles by means of X-ray photoelectron spectroscopy (XPS). The main points of interest in this context are chemical binding states and information on the shell thickness in a non-destructive manner. For this purpose, the  $\text{SiO}_2$  shell thickness systematically was increased while keeping the  $\text{SnO}_2$  core size constant. In case of the desired inhomogeneous ultra-thin  $\text{SiO}_2$  shells low energy ion scattering (LEIS) solely is a suitable means to distinguish between Sn and Si within the outermost monolayer of the spherical particles to prove the attainability of open-pored coatings. In addition, transmission electron microscopy (TEM), X-ray diffraction (XRD), and He-Pycnometry were used to achieve a comprehensive characterization.

<sup>1</sup>B. Schumacher, R. Ochs, H. Troesse, S. Schlabach, M. Bruns, D. V. Szabó, J. Haußelt, Plasma Process. Polym. 4 (2007) 865.

5:20pm **AS-WeA12 Molecular Depth Profiling for Soft Materials by using Size-Selected Large Cluster Ions**, *J. Matsuo, S. Ninomiya, H. Yamada, K. Ichiki, Y. Nakata, T. Aoki, T. Seki*, Kyoto University, Japan

Interest in soft materials, such as polymers or biological materials, has increased in the last decade. SIMS analysis and molecular depth profiling of soft materials with polyatomic and cluster ions have been demonstrated recently. The multiple collisions and high-density energy deposition of these ions on solid surfaces induce enhancement of sputtering and secondary ion yields, as well reduced residual surface damage compared with other techniques. We have demonstrated that the sputtering yields of polymer and amino acids with large Ar cluster ions (mean size: 1000) at the energy of 20 keV are more than 100 molecules/ion, and sputtered surfaces are much smoother than the original surfaces. Secondary ions emitted from arginine (Arg,  $\text{C}_6\text{H}_{14}\text{N}_4\text{O}_2$ ), leucine (Leu,  $\text{C}_6\text{H}_{13}\text{NO}_2$ ), glycylglycylglycine (GlyGlyGly,  $\text{C}_6\text{H}_{11}\text{N}_3\text{O}_4$ ), polymethyl methacrylate (PMMA), and tris (8-hydroxyquinoline) aluminum (Alq3,  $\text{C}_{27}\text{H}_{18}\text{AlN}_3\text{O}_3$ ) films were measured using the time-of-flight (TOF) technique under the incidence of large Ar cluster ions at incident energies of 3 and 20 keV. The ratio of fragment ions to molecular ions decreases quite rapidly with increasing cluster size. Very few fragment ions were observed in the mass spectrum, when the cluster size was larger than 1000. The kinetic energy of a few eV/atom is comparable to the bonding energy of molecules. We have found that residual damage is strongly dependent on the incident velocity of cluster ions, when the size of the cluster ion is larger than 100, and this result is well matched with recent MD simulations. Ultra-low energy SIMS and molecular depth profiling of various soft materials can be realized by using large Ar cluster ions. Recently, molecular depth profiling with low energy (<500eV) monomer ions has also been reported for various polymers. However, in order to realize molecular depth profiling the primary monomer ion beam has to be carefully chosen. The atomistic mechanism of energetic large cluster impacts and the prospects of this technique will be discussed in conjunction with the size effect in secondary ion emission and damage cross-section.

# Authors Index

**Bold page numbers indicate the presenter**

## — A —

Anderson, I.: AS-WeA8, 2  
Aoki, T.: AS-WeA12, 2  
Asakawa, D.: AS-WeA3, 1

## — B —

Baricuatro, J.H.: AS-WeA10, 2  
Bebensee, F.: AS-WeA10, **2**  
Bennett, J.: AS-WeA8, 2  
Brongersma, H.: AS-WeA4, 1  
Bruns, M.: AS-WeA11, **2**

## — C —

Campbell, C.T.: AS-WeA10, 2

## — F —

Farmer, J.A.: AS-WeA10, 2  
Fartmann, M.: AS-WeA11, 2; AS-WeA4, 1  
Fuchs, M.: AS-WeA11, 2

## — G —

Geil, R.D.: AS-WeA9, 2  
Giannuzzi, L.A.: AS-WeA5, **1**  
Gillen, G.: AS-WeA8, **2**  
Gilmore, I.S.: AS-WeA1, **1**  
Gottfried, J.M.: AS-WeA10, 2

Green, F.M.: AS-WeA1, 1  
Grehl, T.: AS-WeA11, 2; AS-WeA4, **1**

## — H —

Hagenhoff, B.: AS-WeA4, 1  
Herzing, A.: AS-WeA8, 2  
Hiraoka, K.: AS-WeA3, **1**  
Hues, S.: AS-WeA8, 2

## — I —

Ichiki, K.: AS-WeA12, 2  
Iijima, Y.: AS-WeA3, 1

## — K —

Kayser, S.: AS-WeA11, 2

## — L —

Lew, W.: AS-WeA10, 2

## — M —

Matsuo, J.: AS-WeA12, **2**

## — N —

Nakata, Y.: AS-WeA12, 2  
Niehuis, E.: AS-WeA4, 1  
Ninomiya, S.: AS-WeA12, 2

## — O —

Ochs, R.: AS-WeA11, 2  
O'Connor, G.: AS-WeA1, 1

## — R —

Rading, D.: AS-WeA4, 1  
Rogers, B.R.: AS-WeA9, 2

## — S —

Sakai, Y.: AS-WeA3, 1  
Schlabach, S.: AS-WeA11, 2  
Schmidt, B.W.: AS-WeA9, **2**  
Seki, T.: AS-WeA12, 2  
Steinrueck, H.-P.: AS-WeA10, 2  
Stokes, P.: AS-WeA1, 1  
Szabó, D.V.: AS-WeA11, 2  
Szakal, C.: AS-WeA8, 2

## — T —

ter Veen, R.: AS-WeA4, 1

## — Y —

Yamada, H.: AS-WeA12, 2

## — Z —

Zhu, J.F.: AS-WeA10, 2