

## Applied Surface Science

Room: C2 - Session AS1-ThM

### Advances in Surface Analysis

**Moderator:** J.A.N.T. Soares, University of Illinois, Urbana-Champaign

8:00am **AS1-ThM1 XPS – A Problem with Charge Referencing Non-Conductive Samples and Native Oxides, V. Crist**, XPS International LLC  
Binding energies (BE) from non-conductive samples and native oxides are commonly charge referenced to the C 1s BE of the hydrocarbon peak of adventitious carbon that appears on the surface of all materials exposed to air. Various studies of the usefulness of this method have been carried out (r.f. P. Swift, *J. Surf. Interfac. Analysis*, p.47, 1982) and none have revealed any significant problem with this everyday practice.

In this talk, C 1s, O 1s and metal spectra and BEs from native and pure binary metal oxides (e.g. MgO or Y<sub>2</sub>O<sub>3</sub>), and a series of residual gas capture studies, will show that there is indeed an obvious and significant problem when this practice is applied to binary metal oxides known to have highly polarized bonds or states (i.e. Al, Cd, Ga, Hf, Mg, Sc and Y). The hydrocarbon C 1s BEs for these native metal oxides routinely appear above 286.0 eV, which is significantly greater than the 284.6-284.8 eV that is commonly used. Another set of native metal oxides (i.e. Ag, Be, Co, Ge, Pb, Si, Zn and Zr) have C 1s BEs: 285.5 eV < C 1s < 286.0 eV.

This higher than expected BE problem is sometimes found for carbon captured by freshly cleaned pure metals exposed (>10 hr) to residual UHV gases and the surface contaminants that adhere to nearby, unclean regions of the sample. The cause of these high BEs might be related to strong surface dipole moments (image potentials) that protrude outward from the highly polarized metal-oxide bonds or states of the metal oxide layer that lie just under the adventitious carbon over-layer. Strong surface dipole moments are predicted (by A. Zangwill, *Physics at Surfaces*, Cambridge Press, 1988) to extend several tens to hundreds of angstroms above the surface of metal oxides into the carbon over-layer and the vacuum, whereas dipoles from pure clean metals are predicted to extend only a few angstroms above the surface.

To demonstrate this problem, spectra from grounded native oxides are compared to native oxides that were floated and irradiated with a flood gun set to OFF, 2 eV and 15 eV (using Mono-XPS). An overlay of five Al 2p spectra (from a 1978 synchrotron study) shows the progressive growth of Al<sub>2</sub>O<sub>3</sub> where the Al 2p BE for Al<sub>2</sub>O<sub>3</sub> = 75.7 eV, **not** 74.3 eV as determined by averaging 42 BEs from pure Al<sub>2</sub>O<sub>3</sub> BE values that are stored in the on-line NIST XPS database of BEs (SRD20). The mean NIST value is ~1.4 eV lower than the 75.7 eV found for native Al<sub>2</sub>O<sub>3</sub> on kitchen foil that gives a 286.3 eV C 1s BE, and also the 75.5 eV found in the 1978 synchrotron study. The experimentally measured 286.3 eV value is 1.5 eV larger than the 284.8 eV value recommended by the NIST database, handbooks and instrument makers.

8:20am **AS1-ThM2 A New Web-Based System for Identifying Molecules and Molecular Structure using G-SIMS and SMILES, I.S. Gilmore, M.A. Phillips, F.M. Green, T.S. Salter, M.P. Seah**, National Physical Laboratory, UK

G-SIMS<sup>[1]</sup> is a powerful method for the identification of organics and complex molecules at surfaces. For complex molecules, evaluating the molecular structure can be key to correct identification. We have shown<sup>[2,3]</sup> that the molecular structure may be reassembled from fragment ions by studying the evolution of G-SIMS intensities as the surface plasma, with effective temperature  $T_p$ , is varied, known as G-SIMS-FPM. Recently, we have developed a novel approach<sup>[4]</sup>, based on SMILES<sup>[5]</sup> (Simplified Molecular Input Line Entry Specification), to assist the reassembly process in an automated way through evaluation of the fragmentation pathways for given molecular structures. A computer program takes a parent structure and goes through every possible fragmentation to provide a tree structure of fragmentation products and simulated fragmentation pathways. For any fragment it is then possible to identify the molecular structure, its mass and a pathway to the parent. We find that there is a good correlation with peak evolution in G-SIMS-FPM data and simulated pathways for two amino acids and a simple peptide. This significantly enhances the application of G-

SIMS-FPM to unknown materials. Once fragmentation pathways have been calculated for a molecule they are added to a library.

We have now developed an informatics database system with a web-based front-end that allows analysts to generate fragmentation pathways for any molecule in SMILES format. For new molecules, the pathways are added to the library. Analysts may then explore the fragment pathways for comparison with the G-SIMS spectra. The free web-based facility allows the library to grow rapidly as use by the community grows. Recent developments in G-SIMS including G-tip technology and the use of cluster ions will be discussed. Examples of the use of G-SIMS and SMILES to identify the structure for different molecules are provided as well as examples of how to use the web-based system.

- [1] I. S. Gilmore and M. P. Seah, *Appl. Surf. Sci.*, 161 (2000), 465.
- [2] I. S. Gilmore and M. P. Seah, *Appl. Surf. Sci.*, 231-232 (2004) 224.
- [3] I. S. Gilmore, F. M. Green and M. P. Seah, *Appl. Surf. Sci.*, 252 (2006) 6601.
- [4] F.M. Green, E.A. Dell, I. S. Gilmore, M.P. Seah, *Int J Mass Spectrom* 272 (2008) 38
- [5] SMILES, Daylight Chemical Information Systems, <http://www.daylight.com/smiles/>.

8:40am **AS1-ThM3 Interrogating Surface Plasmons and Carbon Nanotubes with Four-Wave-Mixing Microscopy, E.O. Potma**, University of California, Irvine **INVITED**

Dual color four-wave-mixing is used to visualize the surface plasmon resonances of individual gold nanowires and the electronic excitations in single carbon nanotubes. The strong nonlinear signals, which are detected at the anti-Stokes frequency, originate from the electronic response of the nanostructures. In gold nanowires, the collective electron motions give rise to strong coherent anti-Stokes signals that can be used to study the orientation and relative strength of the nanostructure's plasmon resonances. In single-walled carbon nanotubes, coherent anti-Stokes contrast can be used to map the orientation and spatial delocalization of electronic excitations in individual nanotubes. Coherent anti-Stokes imaging of the material's electronic response allows for the first close-ups of the coherent nonlinear properties of individual nanostructures and molecules.

9:20am **AS1-ThM5 Observation of Ga<sup>+</sup> Focused Ion Beam Induced X-Rays (FIBIX), L.A. Giannuzzi**, FEI Company, *B.P. Gorman*, Colorado School of Mines

Characteristic X-ray emission from a well grounded metal samples using standard 30 keV Ga<sup>+</sup> focused ion beams is demonstrated. X-ray yields are found to be on the order of 10<sup>-10</sup> per incident ion, consistent with previous studies of low energy, high mass ion – solid interactions. X-ray yields were found to be highest for soft X-rays, i.e., low energy transitions or low atomic number target atoms. Bremsstrahlung X-ray emission was found to be minimal, possibly increasing the detectability limits compared with electron beam induced X-rays. The generation of heavy ion induced X-rays is consistent with a molecular-orbital level crossing model where velocity coupling between the primary ion beam and target atom electrons is not necessary and the majority of X-rays are in fact generated due to recoil effects within the ion – solid interaction cascade.

9:40am **AS1-ThM6 Advances in 2D and 3D TOF-SIMS Imaging of Organics by Means of a C<sub>60</sub> Ion Microprobe and FIB Sectioning, G.L. Fisher**, Physical Electronics, *C. Szakal, G. Gillen*, National Institute of Standards and Technology, *S.R. Bryan*, Physical Electronics

An alternative approach for chemical imaging the interior of an organic specimen is to utilize FIB sectioning. Publications to date concerning FIB sectioning of organic specimens, e.g. simple biological structures, have been restricted to imaging the inorganic species by SEM-EDS. The union of FIB sectioning and TOF-SIMS analysis to achieve chemical imaging has been impeded by the difficulty of collecting secondary ions from the vertical FIB sidewall that is probed by a primary ion beam. Since the ultimate objective involves 3D reconstruction of successive 2D chemical images, it is highly advantageous to perform consecutive sectioning and analysis cycles without moving the sample. This constraint necessitates probing the vertical sidewall of the FIB-milled crater. Therefore, in order to image the vertical sidewall of a FIB-milled crater without moving (i.e. tilting) the sample, the TOF-SIMS analyzer must have characteristics a large depth-of-field and a large solid angle-of-collection. In this presentation, new developments concerning the use of a C<sub>60</sub> ion microprobe and FIB sectioning for advanced characterization of heterogeneous organic materials will be discussed. The advantages and challenges of joining FIB and TOF-SIMS will be demonstrated and discussed. Finally, we will

discuss the application of cluster ion beams to recover the characteristic molecular signals within the FIB-milled area.

10:40am **AS1-ThM9 Temperature Studies on the Induced Molecular Desorption by Atomic and Cluster Projectiles**, *D.A. Brenes, D.G. Willingham*, The Pennsylvania State University, *Z. Postawa*, Jagiellonian University, Poland, *N. Winograd*, The Pennsylvania State University

The temperature dependence in the molecular desorption of coronene films stimulated by 20-keV Au<sub>1</sub><sup>+</sup>, Au<sub>3</sub><sup>+</sup>, and C<sub>60</sub><sup>+</sup> projectiles were experimentally investigated by means of strong field laser photoionization coupled with time-of-flight secondary neutral mass spectrometry (ToF-SNMS) at 300 K and 77 K. The sputtering dynamics of highly energetic ion beams with surfaces have always been assumed to be temperature independent. However, recent data indicate this might not be the case for high energy cluster ion beams.

At 300 K, the kinetic energy distributions of ion beam desorbed coronene neutral molecules are projectile independent. The molecular desorption events stimulated by either projectile are ejected with a most probable translational energy of approximately 0.1 eV and show negligible differences in the high-energy component of the distribution when comparing the projectiles. However, at 77 K the most probable translational energy of ejection is shifted to higher energies as a result of cluster ion bombardment. A most probable translational energy of 0.5 eV is observed when using cluster projectiles such as 20-keV C<sub>60</sub><sup>+</sup>. Fragments created by the C<sub>60</sub> cluster ion sputtering dynamics are detected as low mass fragments at 300 K and exhibit a Maxwell-Boltzmann distribution. This behavior is not evident at 77 K or induced by the other projectiles.

In addition, by comparing the molecular to fragment ion (M/F) signal ratio of well known polyaromatic hydrocarbon photofragments, coronene molecules ejected by 20-keV Au<sub>1</sub><sup>+</sup> exhibit internal energies of sufficient magnitude to reach high energy fragmentation pathways resulting in photodissociation. Similarly, those that were desorbed by 20-keV C<sub>60</sub><sup>+</sup> not only have lower internal energies but the M/F signal ratios are enhanced at 77 K. This investigation suggests the desorption of coronene molecules by C<sub>60</sub> primary ions is dependent on temperature and neutral molecules are ejected with low internal energies under cryogenic conditions.

11:00am **AS1-ThM10 Variation of Carbon Thickness on Magnetic Disk Media: Effects in TOF-SIMS Analysis on Metal Ion Attenuation and Lubricant Spectra**, *A.M. Spool, R. Walzman, R. White*, Hitachi Global Storage Technologies, Inc.

This work continues a previous study<sup>1</sup> on thin overcoat effects on ion attenuation, and the change the proximity of the underlying metal layer has on the spectra of organic materials on top of the carbon. In this study, the overcoat thickness was varied over a larger range than in the previous study, down to bare metal. The samples were measured before and after application of a thin polymer film, a perfluoropolyether commonly used as a lubricant in the hard disk drive industry (Z-Tetraol). The spectra of the lubricant coated samples were explored both for the effect of the lubricant coating on the metal attenuation and for the effect of the varying carbon layer thickness on the lubricant spectra. For this series of samples, the total ion count is expected to vary from sample to sample as it reflects the differences between samples as much as relative individual ion intensities does. Also, the carbon itself produces little signal in TOF-SIMS spectra. The use of a system involving external standards will be described that allows the comparison of spectra from day to day without normalization.

1. Spool, A.; White, R., "Probing Thin Over Layers with Variable Energy / Cluster Ion Beams", *Appl. Surf. Sci.* Volume: 252 Issue: 19 (2006) 6517-6520

11:20am **AS1-ThM11 Large Area Combinatorial Near Edge X-ray Absorption Fine Structure Images: Parallel Process Determination of Molecular Bond Concentration and Orientation on Surfaces**, *D.A. Fischer, C. Jaye*, National Institute of Standards and Technology, *P. Sobol, E.L. Principe*, E.L. Principe & Associates, LLC, *K. Scammon*, University of Central Florida

We show that simultaneous molecular orientation and bond chemistry of large area (18 mm x 13 mm) planar chemically heterogeneous surfaces can be obtained by combining near edge X-ray absorption fine structure (NEXAFS) spectroscopy, a new parallel process magnetic field electron yield optics detector, and a full field incident soft X-ray beam on the sample. The rapid parallel process magnetic field electron yield optics detector (LARIAT: Large Area Imaging Analytical Tool) produces a series of two-dimensional NEXAFS spatial images as the incident soft X-ray energy is scanned above a K or L absorption edge. The image stack reveals information about the chemistry (including bond concentration) and orientation of the surface-bound molecules with 50-micron planar spatial resolution and sub-monolayer molecular sensitivity. The power of the combinatorial imaging NEXAFS method is illustrated by simultaneously

probing the concentration and molecular orientation of single-strand DNA micro array sensors, semifluorinated molecular gradients, and organic electronic combinatorial device arrays. Other possible applications described include the surface orientation and chemistry of continuously graded polymer films and graded or patterned self-assembled monolayers that exhibit tunable surface properties of potential use in nanotechnology. We also envision combinatorial imaging NEXAFS as an insitu probe for catalyst discovery using micro arrays to directly image catalytic chemical activity of thousands of catalysts simultaneously under reaction conditions.

11:40am **AS1-ThM12 The Workfunction Modulation of Al/TiN Bilayer Metal Gate Electrode/High-k Dielectric Gate Stack for NMOS Application**, *E.J. Jung, C.J. Yim, W.S. Im, C.Y. Kim, D.-H. Ko, M.-H. Cho*, Yonsei University, South Korea

In the selection of metal gate electrode material, workfunction is one of the important properties. However, the workfunction tuning of metal gate is more difficult than that of poly-Si gate electrode. The workfunction of poly-Si gate can be tuned by changing dopants and doping concentration, but the workfunction of metal gate shows fixed value because the workfunction of metal is its own characteristic. Thus many research groups have studied bilayer metal stacking methods for tuning interface workfunction between gate dielectric and electrode. In this work, we studied bilayer metal gate stack using Al/TiN bilayer for NMOSFET application, because Al and TiN are commonly used in conventional CMOS process. The high-k dielectric layer (HfO<sub>2</sub>) and gate electrode stack is deposited by ALD and in-situ sputtering system, respectively. The thickness of Al/TiN bilayer was measured by TEM analysis. The workfunction of Al/TiN bilayer gate electrode/high-k dielectric gate stack is measured by backside XPS/UPS depth-profile method. This method is not influenced by gate dielectric type and oxide charge variation. The electrical properties are measured by C-V and I-V measurement methods. The workfunction value of Al/TiN bilayer gate stack was changed between workfunction of Al to workfunction of TiN depending on TiN layer thickness.

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