Applied Surface Science

Room: 610 - Session AS-TuA

3-Dimensional Characterization

Moderator: S.J. Pachuta, 3M Company

1:40pm **AS-TuA1 XPS, TEM, and SIMS Analysis of FIB Bombarded Surfaces Over the Range 500 eV to 30 keV**, ***J.E. Fulghum****, K. Artyushkova,* University of New Mexico*, L.A. Giannuzzi, B. Van Leer, J. Ringnalda,* FEI Company*, F.A. Stevie, D.P. Griffis*, North Carolina State University

Focused Ion Beam (FIB) instruments are known for the ability to provide material removal with a lateral resolution less than 10nm using a Ga+ beam. FIB capabilities continue to improve with low energy performance that allows routine use of glancing angle 2kV Ga+ beams for final polishing of TEM specimens. The lower energy reduces the penetration of gallium into the material under study and minimizes sample damage.[1] It is now routinely possible to reduce the energy of the Ga+ beam to 500eV. Previous work has shown that low energy Ga+ impinging at normal incidence results in Ga deposition.[2] There is also TEM evidence indicating that the use of Ga+ for glancing incidence polishing at energies below 2 keV does not further reduce surface damage in Si, but rather creates a Ga rich region since the sputter yield at these energies drops to a value less than 1.[3] An FIB was used to sputter craters into (100) Si using normal incidence Ga energies from 500eV to 30keV. XPS and SIMS analyses were performed on these craters to determine the Ga surface concentrations and depth distributions at these energies. From 30keV down to 2keV, a decreasing Ga penetration was noted. For the SIMS analyses below 2keV, a surface effect was observed in the SIMS depth profiles which may be the result of an enhancement of silicon secondary ion yield. It my be that glancing incidence polishing at Ga+ energies below 2keV will not result in additional reduction of surface damage. However, the low energy FIB capabilities can provide a means for site specific deposition of Ga when the low energy Ga impinges at normal incidence.

[1]L. Giannuzzi, R. Geurts, J, Ringnalda, Microscopy and Microanalysis Proceedings 11 (Suppl 2) 2005, p.828

[2]D.H. Narum and R.F.W. Pease, J. Vac. Sci. Technol. B6(6) (1988) p. 2115

[3]L. A. Giannuzzi, B. Van Leer, J. Ringnalda, Microscopy and Microanalysis Proceedings (2007).

2:00pm **AS-TuA2 3-D XPS Characterization of Organics Surfaces**, ***J.S. Hammond****, S. Raman, J. Moulder,* Physical Electronics*, N. Sanada, R. Inoue, M. Suzuki*, ULVAC-PHI

For many industrial products, non-uniform surface segregation and contamination of organic constituents on micro-areas of polymeric materials is of great concern. Over the past three years, C60 ion beams have been shown to be very effective for the sputter removal of a surface layer of many organic materials, leaving the remaining surface with minimal chemical damage. By combining a C60 ion gun system with a scanning x-ray microprobe XPS specifically designed for optimum performance for micro-area spectroscopy, chemical state mapping and depth profiling, it is now possible to obtain a three dimensional characterization of organic surfaces. To illustrate this new analytical technique, surface area mapping and micro-area depth profiling of a coated human hair and a micro-area contamination analysis on a thick polymer will be discussed. By using high energy resolution core level spectroscopy as well as valence band chemical state mapping, information on the coating thickness and the spatial dimensions of contamination areas can be obtained. Finally, a comparison between the chemical state damage induced by the C60 ion beam versus the x-ray beam damage during a depth profile will be discussed. Initial experiments indicate that for some polymers, the x-ray beam damage is of greater significance than the chemical changes observed after C60 sputtering. The use of a scanning x-ray beam may facilitate chemical state depth profiling with minimal data artifacts.

2:20pm **AS-TuA3 C60 Molecular Depth Profiling: A Fundamental Study using a 3D Organic System**, ***A.G. Shard****, I.S. Gilmore*, National Physical Laboratory, UK

C_{60} sputtering of organic materials enables the possibility of producing 3 dimensional reconstructions of the distribution of organic compounds. We demonstrate that many organic materials have identical yield volumes (volume sputtered per incident ion) and that, in general, sputtering yield is a well behaved function of ion dose. Irganox layers were created by vacuum evaporation to create well-defined stacks of organic materials with controllable layer thicknesses. These layered materials were employed to determine the energy dependence of sputtering yield, depth resolution and damage accumulation during C_{60} depth profiling. We show that sputtering yield increases with C_{60} ion energy and that depth resolution concomitantly becomes poorer. The multilayers are also used to demonstrate how the depth resolution degrades with depth and a comparison with AFM data shows that the resolution is mainly limited by topography. Examples are also shown of the lateral and depth distribution of mixed organic systems.

2:40pm **AS-TuA4 Prospects for Electron Tomography with Atomic Resolution**, ***C.F. Kisielowski****,* Lawrence Berkeley National Laboratory*, F.R. Chen*, National Tsing Hua University, Taiwan **INVITED**

Since several decades Transmission Electron Microscopy (TEM) is a primary tool for characterizing the inner structure of materials including interfaces and surfaces. A most limiting factor of the transmission-imaging mode comes with the projection of the probed crystal volume into one image plane, which causes loss of information about the materials structure along the electron beam direction. In recent years electron tomography was developed and successfully applied to soft and hard materials yielding the three dimensional materials structure with a resolution that can approach 1-2 nm.[1,2] However, it is still impossible to achieve truly atomic resolution because radiation damage can limit the electron dose and because quantitative procedures need yet to be established that would allow recovering the materials structure at atomic resolution reliably from the recorded images. In order to achieve this goal it is essential to solve the phase problem and to remove effects that relate to the dynamic scattering of electrons in a solid. In this talk we describe current efforts that aim at reaching this goal. Our investigations build on recent hardware and software developments that relate to the DoE's TEAM Project,[3] which will provide a next generation of electron microscopes operating between 80 and 300 kV and providing deep sub Ångstrom resolution. We show that the phase problem is reliably solved and that dynamic scattering can be indeed inverted. As a result a full quantification of the samples mean inner potentials becomes possible, which can be used to determine the number of atoms in each imaged atom column together with its chemical composition. If such experiments are executed along a few zone axes it is possible to reconstruct the atomic structure of materials with atomic resolution.[4] Experimental validations of the developed concept include gold surfaces and bi-crystals of Al:Cu.

[1] C.-E. Hsieh, AR Leith a, C. A. Mannella, J. Frank, M. Marko, Journal of Structural Biology 153 (2006) 1-13

[2] Q. Yang, J. Mardinly, C. Kübel, C. Nelson, C. Kisielowski, International Journal of Materials Research 97, (2006) 880-4

[3] http://www.lbl.gov/LBL-Programs/TEAM/index.html

[4] J.R. Jinschek, H.A. Calderon, K.J. Batenburg, V. Radmilovic, C. Kisielowski, Mat. Res. Soc. Symp. Proc. 839 (2005) 4.5.1 - 4.5.6.

4:00pm **AS-TuA8 Retrospective and Multivariate Statistical Analysis of Three-Spatial-Dimension ToF-SIMS Data Sets**, ***V.S. Smentkowski****, S.G. Ostrowski,* General Electric Global Research*, M.R. Keenan, J.A. Ohlhausen, P.G. Kotula*, Sandia National Laboratories

3 spatial dimension (3D) Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) analysis can be performed if an X-Y image is saved at each depth of a depth profile. We will show how images reconstructed from specified depths, depth profiles generated from specific X-Y coordinates, as well as 3 spatial dimensional rendering provides for a better understanding of the sample than traditional depth profiling where only a single spectrum is collected at each depth. We will also demonstrate that multivariate statistical analysis (MVSA) tools can be used to perform a rapid, unbiased, analysis of the entire 3D data set. Color overlays of the MVSA components and animated movies showing the visualization (in 3D) from various angles will be provided. The MVSA results will also be represented as depth profile traces. 3D ToF-SIMS analysis is performed using only 1 primary ion shot/pixel. Under these conditions, detector dead time effects can introduce non-linearities into the data sets; examples of non-linear data sets will be shown. Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energy's National Nuclear Security Administration under contract DE-AC04-94AL85000.

4:20pm **AS-TuA9 3D Molecular Characterization of a Drug Delivery System**, ***G.L. Fisher****,* Physical Electronics*, A. Belu,* Medtronic Inc.*, K. Wormuth*, SurModics Inc.

Coronary implants that incorporate a drug delivery system are being developed at an increasing rate. It is important for a variety of reasons to characterize such in vivo drug delivery devices and to relate the chemical and physical properties to how the system will function. This study focuses on the characterization of a drug eluting stent coating that consists of

rapamycin in a poly(lactic-co-glycolic acid) (PLGA) matrix. The goal is to understand the lateral and depth distribution of the drug in the polymer matrix. Additionally, the drug distribution is studied as a function of elution time. Information regarding the lateral and depth distribution of rapamycin in PLGA, and the distribution as a function of elution time, was determined by TOF-SIMS depth profiling with a C_{60} cluster ion source. Where appropriate, the TOF-SIMS results will be compared to the results obtained by XPS and confocal Raman. The experimentally-determined 3D chemical structure as a function of elution time, in conjunction with the elution profiles, may be used to enhance the design of future in vivo drug delivery systems.

4:40pm **AS-TuA10 3D Image Acquiring and Spectrum Extraction from 2D Elemental Mapping in Auger Electron Spectroscopy**, ***N. Urushihara****, S. Iida, N. Sanada,* ULVAC-PHI, Inc., Japan*, D.F. Paul, S. Bryan,* Physical Electronics*, M. Suzuki,* ULVAC-PHI, Inc., Japan*, Y. Nakajima, T. Hanajiri*, Toyo University, Japan

Auger electron spectroscopy (AES) is widely used for observation of two-dimensional map (surface elemental distribution) with a high spatial resolution as well as in-depth elemental distribution. An elemental map is generally obtained at an as-received surface or a sputtered surface. Though it is easy to visually recognize elemental distribution in a plane surface, it is difficult to display it three-dimensionally. On the other hand, an energy dispersal spectrum is not stored at each pixel of an elemental map in AES, and it leads a difficulty to investigate spectral shapes at specified points in an elemental map. In order to solve the former issue we have tried to acquire a three-dimensional elemental map and for the latter issue we have studied to extract an energy dispersal spectrum from successive two-dimensional images at fixed kinetic energies. Specimens used were two kinds of SOI (Silicon on insulator) in the study of 3D image acquiring and a part of sputtered crater at the interface region of a silicon dioxide layer on silicon substrate in the study of spectrum extraction from 2D elemental maps. The interface regions were ion-sputtered at the interval of 0.5nm and intensity distributions of Si LVV and O KLL were mapped at a respective depth with 256 x 256 pixels. One can easily recognize three-dimensional features at the interface regions, seeing successive display of 2D maps. It is clearly seen that silicon oxide is formed island structure for the interface in one of the specimens. For the second issue, two-dimensional signal intensities were stored at the region located adjacent to the interface of SiO_2 and Si on a graded sputtered surface. Maps consisted of 64 x 64 pixels and imaged signal intensities were defined as raw intensities including background components. The maps were obtained in the energy ranges of 77 eV to 100 eV for Si LVV with an energy step of 3 eV. At every pixel point energy dispersal spectra were extracted from the 9 maps obtained at the fixed energy. It is obviously distinguished for extracted Si LVV spectra for silicon elemental component and oxide component. All of extracted spectra were processed with linear least square (LLS) method, resulting in separation of elemental and oxide components. In the presentation, results from other material systems for both issues will be demonstrated.

5:00pm **AS-TuA11 Nanospectroscopy of Single Silicon Nanowire Surface using Energy Filtered X-ray PhotoElectron Emission Microscopy (XPEEM)***,* ***O. Renault****, A. Bailly,* CEA-LETI Minatec, France*, N. Barrett, L.-F. Zagonel,* DSM/DRECAM/SPCSI, France*, N. Pauc, P. Gentile,* CEA DRFMC, SiNAPS, France*, **T. Baron***, CNRS-LTM, France

Interest in silicon nanowires (Si NWs) continues to grow, fuelled by novel applications in nanotechnology. This requires precise wire engineering in order to tailor specific surface properties of Si NWs like electron emission properties and surface chemistry, which can be altered by the growth process.[1] Within this perspective, the implementation of novel, non destructive experimental techniques offering both spectroscopic and microscopic capabilities is needed. In this contribution, we present recent results of a surface study using synchrotron radiation induced X-ray PhotoElectron Emission Microscopy (XPEEM) of 250 nm-diameter single NWs dispersed on gold after growth by the Vapour-Liquid-Solid process from gold-silicon catalysts. Here, XPEEM is implemented with the first commercially available NanoESCA spectromicroscope featuring a fully electrostatic PEEM column together with an aberration-corrected energy filter (double hemispherical energy analyser) allowing both a high lateral and energy resolutions.[2-4] The instrument allows laboratory XPEEM experiments with a bright AlKα source, and can also be periodically moved to the European Synchrotron Radiation Facility (ESRF) to benefit from the high brightness and energy tunability of ID08, a soft X-ray beamline.[4] We focus on results related to the energy-filtered, secondary electron images at the photoemission threshold that reveal differences in the local work function and enable investigation, along the nanowire, of the sidewall wetting by the catalyst and the catalyst properties. The double-photoemission threshold shape of the generated nanospectra along the NW surface is a superposition of that characteristic of the Si NW surface and of the gold substrate indicating that gold diffusion and dewetting along the NW sidewall occurs, giving rise to the formation of a non-continuous gold layer. This is confirmed by the Au4f core-level images and SEM observations on the same nanowire. This experiment demonstrates the powerful capabilities of XPEEM nanospectroscopy with the NanoESCA for the surface chemical characterization of single nanostructures.

[1] J.B. Hannon et al., Nature 440 (2006) 69.

[2] M. Escher et al., J. Phys.: Condens. Matter 17 (2005) S1329.

[3] O. Renault et al., Surf. Interface Anal. 2006 ; 38 : 375-377.

[4] O. Renault et al., Surf. Sci. 2007 (in press).

Authors Index

Bold page numbers indicate the presenter

— A —

Artyushkova, K.: AS-TuA1, 1

— B —

Bailly, A.: AS-TuA11, 2
Baron, T.: AS-TuA11, 2
Barrett, N.: AS-TuA11, 2
Belu, A.: AS-TuA9, 1
Bryan, S.: AS-TuA10, 2

— C —

Chen, F.R.: AS-TuA4, 1

— F —

Fisher, G.L.: AS-TuA9, **1**
Fulghum, J.E.: AS-TuA1, **1**

— G —

Gentile, P.: AS-TuA11, 2
Giannuzzi, L.A.: AS-TuA1, 1
Gilmore, I.S.: AS-TuA3, 1
Griffis, D.P.: AS-TuA1, 1

— H —

Hammond, J.S.: AS-TuA2, **1**
Hanajiri, T.: AS-TuA10, 2

— I —

Iida, S.: AS-TuA10, 2
Inoue, R.: AS-TuA2, 1

— K —

Keenan, M.R.: AS-TuA8, 1
Kisielowski, C.F.: AS-TuA4, **1**
Kotula, P.G.: AS-TuA8, 1

— M —

Moulder, J.: AS-TuA2, 1

— N —

Nakajima, Y.: AS-TuA10, 2

— O —

Ohlhausen, J.A.: AS-TuA8, 1
Ostrowski, S.G.: AS-TuA8, 1

— P —

Pauc, N.: AS-TuA11, 2
Paul, D.F.: AS-TuA10, 2

— R —

Raman, S.: AS-TuA2, 1
Renault, O.: AS-TuA11, **2**
Ringnalda, J.: AS-TuA1, 1

— S —

Sanada, N.: AS-TuA10, 2; AS-TuA2, 1
Shard, A.G.: AS-TuA3, **1**
Smentkowski, V.S.: AS-TuA8, **1**
Stevie, F.A.: AS-TuA1, 1
Suzuki, M.: AS-TuA10, 2; AS-TuA2, 1

— U —

Urushihara, N.: AS-TuA10, **2**

— V —

Van Leer, B.: AS-TuA1, 1

— W —

Wormuth, K.: AS-TuA9, 1

— Z —

Zagonel, L.-F.: AS-TuA11, 2