Applied Surface Science
Room: 20 - Session AS-ThA

Applications of Large Cluster Ion Beams - Part 2 (2:00-3:20 pm)/ Surface Analysis using Synchrotron Techniques (3:40-5:40 pm)

Moderator: A.V. Walker, University of Texas at Dallas, C.M. Mahoney, Pacific Northwest National Laboratory, M.L. Pacholski, The Dow Chemical Company, A. Herrera-Gomez, UAM-Azcapotzalco and CINVESTAV-Queretaro, Mexico

2:00pm **AS-ThA1 Applications of a C60 Ion Source for Surface Chemical Analysis: It's Not Just for Polymers**, ***W.F. Stickle****, M.D. Johnson, D. Bilich*, HP

While $C60^+$ ion sources are becoming one of the routinely used tools in the surface chemical analysis laboratory its primary value has been for the study of organic systems. Commonly used for ToF SIMS, the $C60^+$ ion source is also a standard option for photoelectron spectroscopy tools. But many surface analysis laboratories study a wide variety of materials, not just organic thin films, which raises the question as to using this novel ion source for 'routine' analyses. Being able to use of this ion source in a 'routine' fashion requires characterization and understanding of the surface that is being created during the ion milling process. It is important to understand the sputter induced chemistry that may be created by the $C60^+$ source as well as understanding the physical changes that occur to a sample surface during the ion milling. The effects of preferential sputtering, chemical changes or reactions and the nature of surface roughening than can occur will be presented. Several different material systems are examined and discussed with regard to using a $C60^+$ ion gun for enhancing and clarifying 'routine' analyses. The different types of samples to be discussed will include inorganic oxides, multilayer structures as well as metal-metal oxide layered structures and polymers.

2:20pm **AS-ThA2 Towards Ultimate Organic Depth Profiling using Argon Cluster Beams – Recommendations for Dual Beam Profiling and Sample Charge Compensation**, ***R. Havelund****, A.G. Shard, M.P. Seah, I.S. Gilmore*, National Physical Laboratory, UK

The recent innovation of large argon cluster ion sources has revolutionised the ability of SIMS to give 3D chemical images of important classes of organic materials, such as organic electronic materials. Furthermore, sputtering with argon clusters gives the best depth resolution currently achievable of 5 nm [1], constant sputtering yields [2] and minimal chemical degradation [3]. It is clear that this important capability will have major impact in the innovation and manufacture of many advanced technologies. Consequently, there is an urgent need to develop the underpinning metrology. An essential first phase has been the VAMAS interlaboratory study [4] which has highlighted two key issues which we now study in detail. Firstly, the improved depth resolution using argon cluster sputtering and reduced chemical damage reveals effects of the primary beam in a dual beam depth profiling experiment become increasingly important. In this study, we use the Irganox organic multilayer reference material [5] and show that the apparent position of a delta-layer depends on which secondary ion signal is used. It is observed that the delta-layer profiles for small fragment ions appear before the molecular ion profile. The position shift increases with primary beam energy and can be more than 4 nm when a 50 keV Bi_3 ion beam is used. We understand this in terms of a simple sputtering model and provide recommended analytical conditions to reduce this effect. Secondly, it has been widely reported that an initial increase in intensity is observed when depth profiling some organic materials with argon clusters. This is observed for the Irganox reference material and we show this is due electron beam damage from the charge compensation system. Since, typically, lower sputtering yields are used for argon cluster sputtering (owing to the choice of low energy per atom to reduce the sputtering damage) the emitted flux of positive ions is reduced and more electron beam current is required than typically needed using C_{60} sputtering. Previously, we have shown that a maximum limit of $6 \cdot 10^{18}$ electrons per m^2 should be used to spectroscopy [6]. Here, we show that electron damage extends up to 100 nm into the profile. We conduct a systematic study of the electron beam damage as a function of electron dose and energy and give a recommend dose limit.

[1] A.G. Shard et al., This conference

[2] J.L.S. Lee et al., Anal. Chem. (2010), 82, 105

[3] S. Ninomiya et al., Rapid Commun. Mass Spectrom. (2009), 23, 1601

[4] A.G. Shard et al., Surf. Interface Anal. (2011), 43, 1240v

[5] A.G. Shard et al., J. Phys. Chem. B (2008), 112, 2596

[6] I.S. Gilmore and M.P. Seah, Appl. Surf. Sci. (2002), 187, 89

2:40pm **AS-ThA3 Comparative Study of C_{60} and Gas Cluster Ion Sputtering in XPS Depth Profiling for Thin Film Analysis**, ***S.S. Alnabulsi****, J.F. Moulder, S.N. Raman, S.R. Bryan, J.S. Hammond*, Physical Electronics

The objective of successful XPS sputter depth profiling is to accurately identify the layer thicknesses and chemical composition of materials within thin film structures. Cluster ion beam sputtering has been widely used in recent years with the intent to address this essential analytical goal for a broader range of materials, including organic materials. C60 cluster ion beam sputtering provided the first access to quantitative chemical state information below the surface for many polymers, organic and inorganic oxide materials [1].

The recent introduction of argon gas cluster ion beam sputtering to the XPS community has further expanded the capability of successful depth profiling with an emphasis on preserving the chemical structure of challenging polymer and organic materials that exhibit rapid radiation induced damage due to the mobility and reactivity of free radicals that are formed during the sputtering process when other ion sources are used [2].

The purpose of this study is to present a comparative evaluation to quantify the benefits of using either C60 or argon gas cluster ion beam sputtering for XPS compositional depth profiling by characterizing several standard organic and inorganic thin film structures.

N. Sanada, A. Yamamoto, R. Oiwa, and Y. Ohashi, *Surf. Interface Anal.* 36, 280 (2004).

T. Miyayama, N. Sanada, M. Suzuki, J. S. Hammond, S.-Q. D. Si and A. Takahara, *J. Vac. Sci. Technol.* A, 28, No. 2, L1 (Mar/Apr 2010)

3:00pm **AS-ThA4 Damage Profiles of Si (001) Surfaces Bombarded by Ar Gas Cluster Ion Beam**, ***J.G. Chung****, D.J. Yun, Y.K. Kyoung, H.I. Lee, J.C. Lee,* Samsung Advanced Institute of Technology, Republic of Korea, *H.J. Kang*, Chungbuk National University (CBNU), Republic of Korea

The damage profiles of Si (001) surface bombarded by argon gas cluster ion beam (GCIB) and mono-atomic argon ion beam bombardment were investigated using X-ray photoelectron spectroscopy (XPS) and medium energy ion scattering (MEIS). The Ar-GCIB beam was 2 mm in diameter and scanned in an area of 3 mm × 4 mm and the beam current was about 60 nA. The incident angle of the GCIB was fixed at 55° from the surface normal and the mean cluster size was approximately 2500 argon atoms/cluster. The damage profiles of Si (001) bombarded by the Ar GCIB and the mono-atomic Ar ion beam sputtering were measured *ex-situ* MEIS system and *in-situ* MEIS system, respectively. The MEIS results showed that the thickness of the damaged layers on Si(100) is approximately 10 nm for 20 keV, 6.4 nm for 10 keV, and 4.2 nm for 5 keV after the Ar cluster ion dose of 2.3 x 10^{15} clusters/cm^2 and the maximum concentration of the implanted Ar atoms is 0.2 at% for 20 keV and 0.1 at% for both10 keV and 5 keV. The MEIS spectra taken from the Si (001) surface before and after the Ar ion bombardment with the ion dose of 5 x 10^{16} ions/cm^2 showed that the maximum Ar atom concentration was 5.5, 5.8, and 7.8 at% and the damage depth was 5.3 nm, 8.5 nm and 12 nm at 1.0, 2.0, and 3.0 keV, respectively. The depth of the damaged layer is proportional to the in-depth distribution of the implanted primary ions which can be explained in terms of the collision cascade model. Our results showed that the damage did not result from the linear collision cascade for the sample bombarded by Ar GCIB sputtering since the primary cluster Ar atoms were not implanted into the subsurface. The mechanism for the damage generation via the Ar GCIB bombardment is not clear yet, but it should be understood to make it useful for practical applications in solid surface analysis such as SIMS, XPS and AES.

3:40pm **AS-ThA6 Non-Destructive Depth Profiling using VKE-XPS and Maximum Entropy Regularization**, ***C. Weiland****, J.C. Woicik*, National Institute of Standards and Technology

X-ray photoelectron spectroscopy (XPS) is an excellent tool for semi-quantitative analysis of the chemical structure of solid material systems. However, the in-depth distribution of elements in a solid is known to affect the intensity of the measured photoelectron peaks and can thus lead to errors in quantification. The depth distribution itself can be interesting for deposited thin-film systems and buried interfaces. Typically, depth

dependent measurements are made by sputtering layers of the material off the surface, but complications can arise due to knock-on effects, differential sputtering rates and implantation of the sputtering ions. Angle-resolved XPS (ARXPS) coupled with maximum entropy regularization can provide non-destructive depth sensitive information, but analysis is typically performed using a lab-based X-ray source, limiting the ultimate probe depth to tens of Angstroms. Here, we adapt the maximum entropy analysis method used for ARXPS to variable kinetic energy XPS (VKE-XPS) using hard X-rays. Using VKE-XPS with beam energies ranging between 2.1 and 6 keV, we can vary the photoelectron inelastic mean free path to adjust the effective analysis depth to technologically relevant thicknesses. Conversion from intensity vs. beam energy to depth profile can be accomplished using a regularization routine. Development of the routines will be discussed, followed by results of VKE-XPS analysis of plasma-enhanced chemical vapor deposited TiO2 films on Si performed at NIST beamline X24A at the National Synchrotron Light Source.

4:00pm **AS-ThA7 The Early Stage of Corrosion of Cu_3Au Alloy**, ***P. Rajput***, ESRF, France, *A. Gupta,* UGC-DAE Consortium for Scientific Research, India, *C. Meneghini,* Universita di"Roma Tre", Italy, *G. Sharma,* UGC-DAE Consortium for Scientific Research, India, *J. Zegenhagen*, ESRF, France

Metallic alloys are important in our daily life and in industry, but unfortunately highly susceptible to corrosion in wet environment. De-alloying is a particular type of corrosion, attacking alloys which are composed of metals of different "nobility". When coming into contact with an electrolyte, the less noble metal may go into solution, typically causing crack formation and subsequent material failure upon stress. Potential controlled corrosion of a well ordered Cu_3Au crystal in sulfuric acid had been investigated *in situ* [1] showing that, far below the critical potential E_c, at which the alloy is massively dissolved, Cu goes into solution, leaving a ≈ 1 nm thick film of small, Au-rich clusters. Just below E_c, the surface is eventually covered with about 10-20 nm large gold islands with a thickness of 2-3 nm. The Au-rich surface protects the bulk of the alloy against further corrosion (unless E_c is exceeded).

We used, hard x-ray photoelectron spectroscopy (HAXPES), x-ray standing waves (XSW) and depth-selective x-ray absorption fine structure (XAFS) to investigate the very early stages of the corrosion of a more 'realistic', disordered CuAu binary alloy. Ultra-thin Cu_xAu films (2.5 nm, x≈3) were deposited on a Ru/B_4C multilayer to produce the XSW field. The XSW study provides detailed information about the concentration profile of Cu and Au upon de-alloying. HAXPES provides the binding energies (oxidation states) of Au and Cu and XAFS reveals the local atomic structure around Cu and Au.

The pristine Cu_xAu film appeared partially oxidized (CuO and Cu_2O). After dealloying at 245 mV for 2 min in 0.1 M H_2SO_4, the partial Cu dissolution leads to the formation of a Au-rich film with $CuAu_3$-like composition. Quantitative XRF analysis showed that, surprisingly, even below E_c de-alloying leads to the loss of some Au as well.

[1] F. U. Renner, A. Stierle, H. Dosch, T. L. Lee, D. M. Kolb, J. Zegenhagen, Nature 439, 707 (2006).

4:20pm **AS-ThA8 Hard X-ray Photoelectron Spectroscopy (HAXPES) Investigations of Electronic Materials and Interfaces**, ***J.C. Woicik***, National Institute of Standards and Technology **INVITED**

Photoelectron spectroscopy can uniquely measure the chemical and electronic structure of solids and films; however, owing to the generally limiting electron inelastic mean-free path of lab based instruments, the technique is extremely surface sensitive, probing only the first several atomic layers of a given structure. For this reason, synchrotron based hard x-ray photoelectron spectroscopy (HAXPES) in which the photon energy can be varied between 2.1 and 6 keV has emerged as a technique that is ideally suited for studying the electronic and chemical structures of advanced materials systems. In this talk, we will discuss developments of the HAXPES technique at the NIST beamline X24A at the National Synchrotron Light Source for the study of electronic materials. Examples will include nitrogen treatment of HfO2 gate stacks on Si, depth profiling of the HfO2/SiO2 interface, Ga and As "out-diffusion" at semiconductor/oxide interfaces, band offsets and Schottky barrier heights at semiconductor/oxide and diamond/metal interfaces, and oxygen vacancies in N doped TiO2 and solid-oxide fuel cells. In all cases, the increased probing depth of HAXPES over traditional lab based XPS is crucial to study the electronic structure of entire overlayers and/or buried interfaces with thicknesses of industrial significance.

5:00pm **AS-ThA10 Hard X-ray Photoemission Spectroscopy used to Investigate the Resistive Switching Behavior of Manganite Heterostructures: The Case of Ti/$PrCaTiO_3$ Interface**, ***F. Offi,*** CNISM and Dipartimento di Fisica, Università Roma Tre, Italy, *F. Borgatti,* CNR-ISMN, Bologna, Italy, *Y. Yamashita, A. Yang, M. Kobata, K. Kobayashi,* Synchrotron X-ray Station at SPring-8, NIMS, Japan, *C. Park, A. Herpers, R. Dittmann,* Peter Grünberg Institut, Research Center Jülich, Germany, *G. Panaccione*, CNR-IOM, Basovizza-Trieste, Italy

Electrical pulse induced resistance change has been observed at several oxides interfaces but its microscopic origin is still an open issue. In order to shed light on this problem we investigated with hard x-ray photoemission spectroscopy (HAXPES) the interface electronic structure of Ti covered 40 nm $PrCaMnO_3$ (PCMO) film within SrRuO3/PrCaMn03/Ti/Pt devices exhibiting resistive switching behaviour. In particular, we searched for differences arising among the spectra of the virgin (not formed) and the high-resistivity states (HRS). The electronic structure of the Ti top electrode has been probed by measuring the Ti 2*p* spectra. The identification of the Ti 2*p* chemical states on the basis of literature binding energy (BE) values, indicate that the dominant Ti peak at lower BE corresponds to metallic state. Evidence is also found for the presence of Ti(IV) chemical state, due to the formation of TiO_2, and of other intermediate oxide species. Interestingly, the peak corresponding to Ti(IV) is more intense for the HRS than for the virgin state of the samples, suggesting that formation of Ti oxide is induced in the HRS thorough redox reactions related to the migration of oxygen ions from the PCMO inside the Ti layer. Moreover, the core-level spectra of all the elements of the PCMO layer, when compared to the spectra of the reference (uncovered) thick films of these materials, show BE shift and a change of the spectral lineshape that strongly resembles the BE shift dependence of the photoemission spectra on the amount of hole doping, which is related to the change of the chemical potential. Therefore the HAXPES results show changes of the PCMO and Ti electronic structure for this manganite heterostructure, indicating the increment of Ti oxide in the high-resistivity state and pinning of the PCMO chemical potential.

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