

Monday Afternoon, November 13, 2006

Applied Surface Science

Room 2005 - Session AS-MoA

Developing Methods for Data Analysis

Moderator: S. Pachuta, 3M

2:00pm **AS-MoA1 Molecular Structure - G-SIMS with SMILES**, *I.S. Gilmore, F.M. Green, M.P. Seah*, National Physical Laboratory, UK

G-SIMS 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 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 $T_{\text{sub p}}$, is varied, known as G-SIMS-FPM. Here, we develop a novel approach based on SMILES (Simplified Molecular Input Line Entry Specification), to assist the reassembly process through evaluation of the fragmentation pathways of given molecular structures. The SMILES molecular model format allows the molecular structure to be expressed in a logical computer readable way. A computer program has been developed that takes a parent structure and goes through every possible fragmentation providing a tree-structure of fragmentation products. This fragmentation map thus comprises all the possible products without considering relative intensities. For any fragment it is then possible to identify the molecular structure, the mass and the pathway to the parent. By applying this process to many types of parent molecule a foundation library of fragments and pathways is developed. Using G-SIMS-FPM some of these pathways for the unknown molecule can be mapped out. Not all pathways are mapped because some of the fragmentation cascades may be weak and some may only occur for the neutral molecules that are not observed by SIMS. We find that there is a good correlation with peaks in G-SIMS-FPM and the fragmentation maps generated using this approach. The SMILES-based fragmentation maps provide significant help in identifying the molecular structure and this will be illustrated with different complex molecules. @FootnoteText@ @footnote 1@ I. S. Gilmore and M. P. Seah, Appl. Surf. Sci., 231-232 (2004) 224. @footnote 2@ I. S. Gilmore, F. M. Green and M. P. Seah, Appl. Surf. Sci., In the press.

2:20pm **AS-MoA2 Strategies for ToF-SIMS Data Complexity Reduction: A Comparison of G-SIMS and Multivariate Analysis Applied to PLGA Biopolymer Systems**, *F.J.M. Rutten, R. Ogaki*, The University of Nottingham, UK; *S. Li, M. Vert*, University of Montpellier, France; *M.R. Alexander*, The University of Nottingham, UK; *I.S. Gilmore*, National Physical Laboratory, UK; *M.C. Davies*, The University of Nottingham, UK

Amongst the plethora of surface analytical techniques currently available static (time-of-flight) secondary ion mass spectrometry (SIMS) stands out as a very powerful technique capable of yielding highly specific chemical information with often exquisite sensitivity. Information of this kind is more often than not crucial to understand highly complex biomaterial interfaces, such as surface interactions with cells and proteins in anti-fouling or tissue engineering applications. In this paper we present a comparative study of two SIMS spectral analysis approaches applied to a range of copolymers consisting of varying amounts of lactic and glycolic acid. Poly(Lactic-co-glycolic acid) (PLGA) is biodegradable and as such currently in use in a number of applications in the biomaterials field, such as tissue engineering scaffolds and drug delivery systems. A drawback of SIMS relates to the rather violent process involved in the generation of diagnostic secondary ions, which involves the impact of highly energetic ions leading to the formation of a range of charged fragments for a single molecular species. Whereas a wealth of information is captured in the resulting mass spectra, their complexity often precludes interpretation of all but the most prominent fragments. At present two approaches show great promise in reducing the complexity of SIMS spectra, thus maximising extractable information: Gentle-SIMS (G-SIMS) uses acquired data with different levels of fragmentation to extrapolate to lower surface plasma temperatures and hence amplifies otherwise weak but highly diagnostic larger mass fragments (e.g. Ref. 1). Multivariate analytical approaches reduce complexity by generating new variables which contain the most pertinent parts of spectra, with the possibility to relate this to surface chemistry. The relative merits of both techniques are discussed for PLGA-drug systems. @FootnoteText@ @footnote 1@ I.S. Gilmore, M.P. Seah, Appl. Surf. Sci. 231-232 (2004) 224 and refs. therein.

2:40pm **AS-MoA3 Multivariate Analysis of Correlated Spectral Images**, *J.A. Ohlhausen, M.R. Keenan, P.G. Kotula*, Sandia National Laboratories; *V.S. Smentkowski*, General Electric Global Research Center **INVITED**

Spectral imaging is a very powerful approach for collecting large amounts of potentially very useful data needed to characterize a material surface. The challenge arises with analyzing the large data sets in an unbiased way. This challenge can be overcome for single spectral images using multivariate statistical analysis (MSA) methods developed at Sandia. This presentation describes the application of MSA to the even greater challenge of correlated analyses. Specific examples that will be described include: Correlating positive-ion TOF-SIMS spectral images from multiple specimens comparing different process conditions; Correlating TOF-SIMS spectral images in the depth dimension to perform comprehensive 3D analysis; Correlating positive and negative TOF-SIMS spectral images from the same areas of a specimen; Correlating TOF-SIMS and electron-excited x-ray spectral images; and finally the correlation of XPS spectral images with Valence Band spectral images. Remaining challenges and pitfalls in correlated single- and multiple-technique spectral image analyses will also be discussed. 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.

3:20pm **AS-MoA5 X-ray Photoelectron Spectroscopy (XPS) Multi-Spectral Imaging of Aluminum Alloy Surfaces using Principle Component Analysis**, *C.H. Lee*, University of Manchester, UK, United Kingdom; *J. Walton, G.E. Thompson*, University of Manchester, UK; *M.R. Alexander*, University of Nottingham, UK

Aluminum alloys are of technological importance in most market sectors, ranging from architecture through aerospace to electronics products. Consequently, such alloys are the subject of much interest, particularly the near-surface and surface properties, which influence behaviour such as corrosion and adhesion of subsequent coatings. The aim of this study is to spatially resolve constituent particles in selected aluminium alloys and to disclose their contributions to the adsorption of a self-assembled flourinated alkyl phosphonic acid ($C_{10}F_{21}CO_2H$). Thus, XPS images have been obtained at small energy steps on both AA2024 T3 and AA6016 T4 aluminium alloys to maximize the acquired spectral information, which has been extracted using a multivariate statistical analysis approach (MVA) consisting of singular value decomposition (SVD) and principal component analysis (PCA). @footnote 1@ As a result, noise-reduced and background-corrected multispectral imaging has revealed the constituent second phase particles in the respective alloy systems, the particles distribution has been correlated with scanning electron microscope (SEM) and optical microscope images. Comparison of the surfaces before and after in-situ argon ion etching indicated preferential oxidation of aluminium formed with a copper enriched phase immediate beneath the oxide layer in the AA 2024 T3 aluminium alloy. As for, AA 6016 T4 aluminium alloy, the behaviour of Al-Fe-Si and Mg₂Si particles has been compared. The previous finding has been used to examine the chemisorption of flourinated alkyl phosphonic acid self-assembled layer onto the oxidised alloy systems. The multispectral XPS images show that the molecule assembled relatively uniformly on the 2024T3 compared to a heterogeneous distribution observed on the 6016T4. @FootnoteText@ @footnote 1@ J. Walton and N. Fairley J. Electron Spectrosc. Relat. Phenom. (2005) 148 29-40.

3:40pm **AS-MoA6 High Spatial Resolution XPS and AES Applied to the Understanding of Interfacial Delamination in Microelectronics**, *H. Piao, L. Le Tarte*, General Electric Co.; *N. Fairley*, Casa Software Ltd.

X-ray Photoelectron Spectroscopy (XPS) and Auger Electron Spectroscopy (AES) are the most widely used techniques for quantitative surface analysis. XPS is mainly dedicated to the identification of chemical composition/bonding on surfaces, while the high spatial resolution in AES has made it an established technique for determining the localized defects or other features distributed on surfaces. Although the spatial resolution in XPS has been much inferior to that in AES, the recent development of XPS instrumentation with near-micron spatial resolution has advanced the capability of elemental and chemical state imaging accompanied by small area analysis. @footnote 1@ The goal of this presentation is to show how the combined uses of XPS and AES at enhanced spatial resolution have significantly improved the understanding of interfacial delamination and related problems encountered in the production of electronic devices in the field of microelectronics. A few examples of the application of surface

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analysis for adhesion problems will be presented. In the presentation, the mathematical procedure using Principle Component Analysis (PCA) in the reduction of noise in XPS images² will also be described. The purpose of the PCA is to identify the abstract factor images containing significant information and reconstruct the images only using these factors without noise, therefore resulting in the set of images with enhanced signal-to-noise. The dramatic improvements in the image contrast and chemical component determination from multi-spectral image data sets will be demonstrated. ¹D. Briggs and J.T. Grant, *Surface Analysis by Auger and X-ray Photoelectron Spectroscopy*, Surface Spectra/IMPublications, 2003.²N. Fairley and A. Carrick, *The Casa Cookbook*, Acolyte Science, 2005.

4:00pm AS-MoA7 Structure Elucidation of Nano-Composite Catalysts by Multivariate Analysis and Regression Modeling of XPS Data, K. Artyushkova, J.E. Fulghum, T.S. Olson, P. Atanassov, University of New Mexico

A new class of non-platinum electrocatalysts, based on pyrolysed porphyrins), was studied using X-ray photoelectron spectroscopy (XPS) in combination with multivariate analysis. Understanding the CoTMPP electrocatalyst structure in combination with surface medications occurring during pyrolysis requires identification of subtle changes in a very complex system. Deconvoluting numerous overlapping photoelectron peaks is a particular challenge in this case, as new species formed during pyrolysis may appear at the same binding energy as existing species. High-resolution spectra acquired from the precursor and electrocatalysts pyrolyzed at various experimental conditions were curve-fit using a) individual peaks of constrained width and shape as well as b) experimentally obtained photopeaks from the precursor and additional peaks required for a complete curve fit. Principal Component Analysis (PCA) was applied to quantitative results from the curve-fits of both types of spectra of pure elements, and various combinations, to identify types of species both formed and destroyed during the pyrolysis process and to find correlations between them. It was established that the catalyst presents a nano-composite of highly dispersed pyropolymer with remaining Nx-centers inserted in a graphite-like matrix. Approximately 50% of the metal is Co²⁺ associated with remaining N₄-centers. The remaining cobalt is present in crystallites of metallic Co, coated with thin layer of CoO. The distribution of these types of moieties is directly related to the efficiency of oxygen reduction. A Spectra-to-property relationship was developed by applying multivariate regression models correlating XPS data with rotating-ring disk electrode (RRDE) data for the CoTMPP catalyst treated in various acids which selectively remove chemical moieties. These models have a potential for predicting the chemical composition of the CoTMPP catalyst which optimizes electrochemical performance.

4:20pm AS-MoA8 Attenuation Lengths for Measurement of SiO₂ Film Thicknesses by XPS, C.J. Powell, National Institute of Standards and Technology; W.S.M. Werner, W. Smekal, Technical University of Vienna, Austria

Effective attenuation lengths (EALs) are needed for measurement of film thicknesses by XPS, and have often been obtained from the NIST Electron Effective-Attenuation-Length Database.¹ These EALs are derived from a model in which it is assumed that the substrate and the overlayer film have the same electron-scattering properties. We have used the new NIST Database for the Simulation of Electron Spectra for Surface Analysis (SESSA)² to compute EALs for thin films of SiO₂ on Si. With SESSA, the actual scattering properties for each material are utilized, and the resulting EALs are considered more reliable. EALs have been calculated for two emission angles and several film morphologies to simulate recent careful experiments:³ (a) an SiO₂ layer of variable thickness (1.4 nm to 7.6 nm) on Si; (b) an SiO₂ layer of variable thickness and three thin intermediate suboxides on Si; (c) a carbonaceous layer, an SiO₂ layer of variable thickness, and three intermediate suboxides on Si. The new EALs show a larger variation with SiO₂ thickness than found previously.⁴ The implications of these results for SiO₂ thickness metrology will be discussed. ¹<http://www.nist.gov/srd/nist82.htm> ²<http://www.nist.gov/srd/nist100.htm> ³M. P. Seah and S. J. Spencer, *Surf. Interface Anal.* 37, 731 (2005). ⁴C. J. Powell and A. Jablonski, *J. Vac. Sci. Tech. A* 19, 2604 (2001).

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