Applied Surface Science
Room 206 - Session AS-FrM

Practical Methods and Applications for Surface Analysis

Moderator: M.C. Burrell, GE Global Research Center

8:20am **AS-FrM1 ToF-SIMS Measurements of a Fluorocarbon-based Self-Assembled Monolayer on Si***, **J.A. Ohlhausen**, K.R. Zavadil,* Sandia National Laboratories

Low surface energy coatings and films are needed to minimize stiction, high friction and wear of the oxide-terminated silicon-based MicroElectroMechanical Systems (MEMS) to ensure reliable device function. One common approach is to deposit self-assembled monolayer (SAM) films containing reactive silane headgroups and low energy pendant chains to cover the complex structures used in MEMS devices. The composition of these films is difficult to characterize and quantify (a property or quality is quantified composition, an aspect of structure, etc.). Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is an ideal tool for characterizing these types of films, however interpretation of the spectral data generated is complex and challenging. We are using the combination of X-ray Photoelectron Spectrometry (XPS) and ToF-SIMS to detect and quantify several candidate fluorocarbon-based SAMS on Si coupons and on MEMS devices. Unexpected fragmentation caused by the interaction of the primary ion beam with the fluorocarbon chain in contact with the Si surface creates ions whose presence are not intuitive. We can account for these ion fragments and use them to aid in quantifying the film composition. Our methods include the use of coverage-dependent fragmentation signatures along with the application of multivariate statistical techniques to establish the co-variance in these signatures. The fragmentation seen in this system along with the quantification method we used will be presented. @FootnoteText@ Sandia is a multiprogram laboratory operated by Sandia Corporation, a Lockheed Martin Company, for the United States Department of Energys National Nuclear Security Administration under contract DE-AC04-94AL85000.

8:40am **AS-FrM2 XPS-imaging; Investigation of the Potentials of a Recent Algorithm Applied to a Patterned Polymer***, S. Hajati,* University of Southern Denmark*; S. Tougaard,* University of Southern Denmark, Denmark*; **S.J. Coultas**, C.J. Blomfield, C. Moffitt,* Kratos Analytical Ltd, UK

We have investigated the practical potentials of a recent algorithm for automatic data processing of XPS spectra.@footnote 1@ For each XPS peak, this algorithm determines the total amount of the corresponding atoms within the outermost ~ 3 inelastic electron mean free paths and it also gives an estimate of their depth distribution. The validity of the algorithm was recently tested@footnote 2@ by analysis of conventional (low lateral resolution) XPS measurements from layered samples. It was found to be very accurate and robust and much superior to usual analysis which relies on peak areas. In this paper we have studied spectra acquired at high lateral resolution (~2µm) of a patterned hydrophilic plasma polymer deposited on to a PTFE substrate. The spectra are reconstructed from a series of parallel photoelectron images recorded using a pulse counting delay line detector. For each pixel, we have used the C1s, F1s and O1s peaks to determine the amount of atoms as well as their approximate depth distribution for each element. The method is less accurate than the traditional QUASES-peak shape analysis method. However the latter requires operator interaction and is not practical for XPS imaging where thousands of spectra must be analyzed. @FootnoteText@ @footnote 1@ S. Tougaard, J. Vac Sci. Technol. A21, 1081 (2003)@footnote 2@ S. Tougaard, J. Vac. Sci. Technol. 2005, In press .

9:00am **AS-FrM3 Surface Analysis in Modern Industry - More, Faster, Cheaper, Better?***, **I.W. Fletcher**, S.F. Davies,* ICI plc, UK **INVITED**

The driving aim of most industrial activity is to make money by producing and selling products that people need or want and many processes and products involve surfaces or surface chemistry issues where surface analysis can deliver significant benefits. Research and development along with process and product problem solving are the obvious areas, although SHE, patent protection and various legal applications are also important. There is pressure on most businesses to increase profitability and to reduce costs, with analysis all too often being seen as pure cost. The 'do more, faster, cheaper' requirement may seem to conflict with the unwritten requirement to 'do it right'. Industrial analytical problems can and do provide significant challenges, often pushing analysts, instrumentation and techniques to the limits of what is possible. Fortunately modern equipment is now more reliable, often automated and is also capable of producing better quality data with much higher signal to noise levels and with better resolution than before. These help with the speed and accuracy of analysis and also open up new areas of information that were previously inaccessible. For example, images of the various species on the surface can be critical to a complete understanding of the situation and to many product developments. Using static SIMS with polyatomic and cluster ion beams, it is now routinely possible to generate images from truly molecular species rather than from elemental or small fragment ion species. This presentation will outline several practical examples using SSIMS and XPS applied to 'industrial' samples including man-made fibres, hair, foodstuffs and catalysts.

9:40am **AS-FrM5 Comparison of Methods for the Quantification and 3D Characterization of Polymer Blends using XPS and CLSM***, **J.L. Fenton**, K. Artyushkova, J.E. Fulghum,* University of New Mexico

The complete characterization of a heterogeneous polymer blend often requires multiple analytical techniques; each of the techniques providing limited data compared to the total information required. The most effective approach to multitechnique analysis utilizes data acquired from the same area on the same sample. However, there are still a number of issues to be resolved if quantitative multitechnique fusion is to be utilized. This study evaluates methods for quantifying phases observed in confocal laser scanning microscopy (CLSM) images. CLSM images can have a lateral resolution comparable to or better than XPS images, provide information on fluorescent polymer phase distribution, and 3D volumes can be created by changing the focal plane. In this talk we evaluate the use of CLSM images to quantitatively investigate phase distributions in polymer blends as a function of depth. CLSM image quantification methods including using image intensity calibration beads with vertical polymer blend distribution standards, analytical treatment of CLSM optics and fluorescence properties, and correlation with XPS images are compared. The quantitative concentration data is then used to create a 3D volume containing chemical and elemental concentration information. This work has been partially supported by NSF CHE-0350666, the UNM NSF IGERT CORE DGE-00114319 and UNM.

10:00am **AS-FrM6 X-ray Photoelectron Spectroscopic Study of an Oxygen-doped Zinc Sulfide Surface Using Sample Biasing***, **Y.-Q. Wang**, P.M.A. Sherwood,* Oklahoma State University

X-ray photoelectron spectroscopy (XPS) was used to study the surface chemistry of zinc sulfide (ZnS) exposed to a number of oxidation treatments at various conditions to understand the effect of oxygen on surfaces of II-VI compounds. These compounds are widely used as luminescence and window materials, where the mechanism of the effect of oxygen interaction and its effect on the properties and applications of these materials, has not been clearly understood. The oxygen was introduced onto the ZnS surface by heat-treating the sample in a furnace with water vapor and by synthesis of ZnS. The core XPS studies were conducted with and without the application of a sample bias potential, and showed that oxygen interaction caused a considerable change in the surface chemistry of ZnS. The application of a positive bias led to a shift in the core XPS peaks expected for a conductive material, but the negative bias gave rise to unusual behavior. In the case of ZnO the core XPS peaks behaved in the way expected of a conducting material under positive or negative bias. The ZnS samples exhibited a peak shift that was closely related to the oxygen content in the surface region. Furthermore, the sample synthesized in aqueous solution resulted in peak splitting under a negative bias. The surface chemistry monitored by XPS, and the interpretation of the biasing shifts allows for a better understanding of the change of luminescence phenomena in ZnS materials involving oxygen.

10:20am **AS-FrM7 Thin Oxide Free Phosphate Films of Novel Composition formed on the Surface of Vanadium Metal and Characterized by X-Ray Photoelectron Spectroscopy***, D.J. Asunskis, **P.M.A. Sherwood**,* Oklahoma State University

This paper reports the preparation of thin (less than 100 Angstroms) oxide-free phosphate films of various compositions on vanadium metal. These films are interesting because of their potential for corrosion inhibition, adhesion promotion and biocompatibility. Valence band and core-level X-ray photoelectron spectroscopy (XPS) were used to characterize the films. The valence band spectra obtained were compared with spectra generated from band structure calculations for various vanadium phosphates and from previously reported spectra of vanadium phosphates. Novel vanadium phosphate coatings were created by the reaction of vanadium metal and different phosphorus-oxygen containing acids, H@sub 3@PO@sub 4@, H@sub 3@PO@sub 3@, H@sub 3@PO@sub 2@ and H@sub 4@P@sub 2@O@sub 7@. The paper focuses upon the valence

band region which shows significant differences between the three vanadium phosphate films formed as well as clear differences between the three phosphates and vanadium oxides. The valence band spectra are effectively interpreted by band structure calculations. @FootnoteText@ The work was supported by the National Science Foundation under Grant No. CHE-0137502.

10:40am **AS-FrM8 Surface Characterization of Metal Exchanged Mesoporous Materials*, S.G. MacKay*,** University of Maine, US*; K.D. Bishop, B.K. Schaefer, J.D. Anderson, J.C. Bolton, H.H. Patterson,* University of Maine

We are investigating the role of transition metal clusters in heterogeneous photocatalysts used for the remediation of a variety of toxic organic compounds. These catalysts have already been successfully employed in remediating organophosphorous and carbamate compounds,@footnote 1@ and they have also been shown to be robust in the presence of dissolved organic carbon.@footnote 2@ The design of these catalysts involves incorporating metal ions into mesoporous materials via ion exchange. Manipulation of the support material geometry and the metal ion composition provides control over the catalyst selectivity and reactivity. Currently we are expanding our application areas to include biological target molecules and organisms. For these studies we have covalently attached zeolite and MCM photocatalysts onto a polymer surface using a methacryl silane. XPS was used to study both the catalyst/polymer attachment chemistry as well as the surface oxidation states of the photocatalytic metal sites. Catalysts studied include faujasite zeolites at different Si/Al ratios exchanged with Ag as well as with mixed metals (Ag/Cu). The correlation of these results with earlier published work using photoluminescence will be shown along with data from both TOF-SIMS and high resolution TEM analyses of these same materials. @FootnoteText@ @footnote 1@J. Phys. Chem. B. 2001, 105, 7508-7516.@footnote 2@Envir. Sci. Technol. 2003, 37, 2280.

11:20am **AS-FrM10 Improving High Resolution AFM Images - When are Sharp Tips Worthwhile?*, C.F.H. Gondran,*** ATDF Inc., a subsidiary of SEMATECH*; D.K. Michelson,* ISMI, a subsidiary of SEMATECH

Recently, AFM probes with sharper tips (1-2 nm radii of curvature) have become commercially available. This provides broad access to an opportunity to improve high-resolution images. Under the right circumstances, these improvements are very dramatic.@footnote 1@ However, in other instances, sharp tips offer limited benefits and the additional cost may not be justified. This study is designed to improve our understanding of the benefits of using sharp tips and to help determine when these benefits can be realized. Two-dimensional geometric models@footnote 2@ are used to evaluate the effect of tip shape on AFM images, roughness values, and power spectral density curves obtained for a variety of sample types. The effects of tip size are studied as a function of the sample's surface roughness, average feature size, average feature spacing, and surface feature shape. The results, particularly for roughness values, are not always intuitive. The simulated data are correlated to sample data obtained on films commonly used in research and development for semiconductor manufacturing: epitaxial Si, high-k, low-k, and barrier layer materials. These correlations are used to assess the value of sharp tips for the semiconductor industry. @FootnoteText@ @footnote 1@ D. Klinov, S. Magonov "True molecular Resolution in Tapping-Mode Atomic Force Microscopy with High-Resolution Probes," Applied Phys. Letts., 84(14) 2004, p. 2697.@footnote 2@ C. F. H. Gondran, D. K. Michelson "Sampling and Reference Considerations for Very High Resolution AFM Analysis," in Proc. 30th International Symposium for Testing and Failure Analysis, ASM International, Ohio, 2004 p. 357.

11:40am **AS-FrM11 Microscopy Study of Composites Based on Propylene-Ethylene Copolymers*, L.L. Ionescu-Vasii*,** *P. Wood-Adams,* Concordia University, Canada*; E. Duschene,* Ecole Polytechnique de Montréal, Canada

MMany recent developments in polymer materials science have been triggered by the development of improved synthesis methods. As a consequence, a wide variety of polymers with unusual properties can be designed and synthesized. Recently, The Dow Chemical Company developed a new catalyst which allows copolymerization of propylene with various alpha-olefin comonomers over a broad range of compositions in isotactic fashion and with high molecular weight (SWOGGER K et al, 2003). Our interest focuses on a new family of propylene-ethylene copolymers produced by Dow Company, which has an exceptional ability to accept very high loadings (80% wt and higher) of fillers or/and additives, while maintaining good processability. The new propylene-ethylene (P/E) copolymers used in our study exhibit high molecular weights, low densities, relatively narrow molecular weight distributions and unique micro-molecular structures. The ethylene content of these copolymers ranges from 9 to 15 wt %. We report here the first results of our microscopy study of twelve composites (with 20, 40, 60 and 80 wt% calcium carbonate filler) based on three new propylene-ethylene copolymers. Different microscopy techniques (SEM, TEM, AFM) and different samples' preparation techniques (cryogenic microtomy, FIB, annealing) were used in order to obtain a thorough understanding of the microstructure of the composites studied and to evaluate the interaction between the filler particles and the polymer matrices. @FootnoteText@ @footnote 1@ SWOGGER K. W., POON B., ANSEMS P., CHUM S., HILTNER A. AND BAER E. (2003), Material classification and applications of new propylene-ethylene copolymers. SPE ANTEC Tec. Papers, 1768.

Author Index

Bold page numbers indicate presenter

— A —
Anderson, J.D.: AS-FrM8, 2
Artyushkova, K.: AS-FrM5, 1
Asunskis, D.J.: AS-FrM7, 1
— B —
Bishop, K.D.: AS-FrM8, 2
Blomfield, C.J.: AS-FrM2, 1
Bolton, J.C.: AS-FrM8, 2
— C —
Coultas, S.J.: AS-FrM2, **1**
— D —
Davies, S.F.: AS-FrM3, 1
Duschene, E.: AS-FrM11, 2
— F —
Fenton, J.L.: AS-FrM5, **1**
Fletcher, I.W.: AS-FrM3, **1**
Fulghum, J.E.: AS-FrM5, 1
— G —
Gondran, C.F.H.: AS-FrM10, **2**
— H —
Hajati, S.: AS-FrM2, 1
— I —
Ionescu-Vasii, L.L.: AS-FrM11, **2**
— M —
MacKay, S.G.: AS-FrM8, **2**
Michelson, D.K.: AS-FrM10, 2
Moffitt, C.: AS-FrM2, 1
— O —
Ohlhausen, J.A.: AS-FrM1, **1**
— P —
Patterson, H.H.: AS-FrM8, 2
— S —
Schaefer, B.K.: AS-FrM8, 2
Sherwood, P.M.A.: AS-FrM6, 1; AS-FrM7, **1**
— T —
Tougaard, S.: AS-FrM2, 1
— W —
Wang, Y.-Q.: AS-FrM6, **1**
Wood-Adams, P.: AS-FrM11, 2
— Z —
Zavadil, K.R.: AS-FrM1, 1