

Tuesday Afternoon, October 31, 2017

Applied Surface Science Division

Room: 13 - Session AS+TF-TuA

Problem Solving Using Surface Analysis in the Industrial Laboratory

Moderators: Jeffrey Fenton, Medtronic, Paul Vlasak, The Dow Chemical Company

2:20pm **AS+TF-TuA1 TOF-SIMS MS/MS for Industrial Problem Solving**, G.L. Fisher, D.M. Carr, Physical Electronics, T. Miyayama, S. Iida, ULVAC-PHI, Japan, **Scott Bryan**, Physical Electronics

One of the most common requests in an industrial analytical lab is to distinguish between “good” and “bad” samples of supposedly the same composition. For failure analysis labs, the goal is often to determine the source of contamination or defects in a production process with poor yield. Identifying contamination left behind from different cleaning procedures or after extended use is also a common request. In all these circumstances, one does not know ahead of time what chemical compounds are present. TOF-SIMS is an ideal technique for these applications because it has high sensitivity, high specificity, and parallel detection of all masses. One complication is that real-world samples usually have a complex mixture of compounds on the surface, making the TOF-SIMS spectrum difficult to interpret. Further, the use of a wide variety of different primary ion beams (e.g. Ga⁺, In⁺, Au⁺, Bi⁺, C₆₀⁺, and Ar_n⁺) has complicated the use of TOF-SIMS spectral databases for compound identification due to large changes in relative peak intensities from one beam to another.

A MS/MS capability was recently integrated into a TOF-SIMS instrument to make compound identification easier [1,2]. It allows unambiguous identification of both organic and inorganic peaks above *m/z* 200, where the mass accuracy is insufficient to identify the composition of a peak by its exact mass. A MS/MS spectrum from a single precursor mass is much easier to match using a spectral database compared to using the original complex TOF-SIMS spectrum. In addition, the MS/MS spectrum of a given precursor ion is independent of the primary ion used to generate it.

Several case studies will be given where MS/MS was needed to identify compounds from an analysis of industrial samples. Two modes of MS/MS will be compared and contrasted. One is based on collision induced dissociation (CID) with inert gas and the other is based on post source decay (PSD).

[1] G.L. Fisher, J.S. Hammond, P.E. Larson, S.R. Bryan, R.M.A. Heeren, J. Vac. Sci. Technol. B 34(3), 2016, 03H126-1.

[2] G.L. Fisher, A.L. Bruinen, N. Ogrinc Potočnik, J.S. Hammond, S.R. Bryan, P.E. Larson, R.M.A. Heeren, Anal. Chem., 88, 2016, 6433-6440.

2:40pm **AS+TF-TuA2 In Situ Molecular Imaging of Switchable Ionic Liquids**, Juan Yao, D. Lao, X.F. Yu, S. Nune, D. Heldebrant, Z.H. Zhu, X.Y. Yu, Pacific Northwest National Laboratory

Switchable ionic liquids (SWILs) are emerging green solvents in industry for cleaner separation and efficient biomass production, for instance. However, the liquid structure and composition of SWILs are not fully understood. Besides some off-line analyses using NMR and IR, our knowledge of the SWIL is quite limited. We used in situ liquid time-of-flight secondary ion mass spectrometry (ToF-SIMS) to study SWILs in this work. SWILs are introduced into a vacuum compatible microfluidic channel for analysis by liquid SIMS. Two model systems have been investigated. The first consists of 1, 8-diazabicycloundec-7-ene (DBU) and 1-hexanol with different CO₂ loadings. The second is primarily made of koechanol with various CO₂ loadings. Koechanol acts as both acid and base in the latter. Our results show two coexisting liquid phases in the two SWIL systems. This phenomenon was only hypothesized in previous theory prediction. We are able to provide the first physical evidence of the complex liquid-liquid interface using three-dimensional chemical mapping with submicrometer resolution. In addition, more complex stoichiometry is discovered as a result of SWIL formation. More importantly, we provide the first chemical spatial mapping elucidating the evolved liquid-liquid interface as a result of SWIL formation. We anticipate the more detailed molecular level understanding of the liquid structure and composition are instrumental to build the foundation for predictive material synthesis and more versatile industrial applications.

3:00pm **AS+TF-TuA3 Employing a Surface and Bulk Analytical Approach for the Synthesis and Characterization of Ophthalmic Biomaterials**, Daniel Hook, A. Hoteling, W. Nichols, I. Nuñez, K. Wygladacz, Bausch + Lomb, Inc. **INVITED**

Background:

During the development of a new soft contact lens material three areas of focus; regulatory requirements, manufacturing requirements and customer needs, are often used to guide the overall activities of the material development process.

Regulatory requirements are associated with material properties that are collected using methods defined by standards organizations and accepted by regulatory bodies globally. While this data is mandatory for the registration and approval of a contact lens material it is incomplete in that it only defines the basics of the material.

Manufacturing requirements such as speed of polymerization and completeness of reaction provide critical information so that an effective material can be made in a cost effective manner.

Finally, patients will demand a material that can be worn comfortably while correcting vision over the course of the wearing schedule. Patient focused parameters such as incorporation of wetting agents that create a wettable surface as well as a robust surface that will withstand handling of the course of several weeks of wear area also critical to success.

Methods:

The ISO methods 18369-4:2006, 4.6, 18369-4:2006, 4.4, 18369-4:2006, 4.5 were used to collect bulk properties of water content, oxygen permeability and refractive index while ANSI method Z80.20.2010, 7.10 was used to collect captive bubble contact angle data (CBCA). Photo-Differential Scanning Calorimetry (Photo DSC), Gas Chromatography-Mass Spectrometry (GC-MS) and Liquid Chromatography - Mass Spectrometry (LC-MS) were used to measure polymerization kinetics and monomer consumption. X-ray Photoelectron Spectroscopy (XPS) data was collected to understand surface uniformity and product consistency while Atomic Force Microscopy (AFM) was used to assess surface morphology over the course of the wearing schedule.

Results and Conclusion:

Data summarizing the submission for samfilcon A, a 46% water, 114 Dk material will be presented. CBCA coupled with XPS data will demonstrate a consistent surface wettability and chemistry across multiple lens powers and lens lots. Photo DSC, GC-MS and LC-MS will illustrate how the lens polymerizes in two distinct time resolved phases enabling the incorporation of polyvinyl pyrrolidone wetting agent into the lens bulk and surface. Together the analytical data will provide a unique picture of the data set needed for regulatory approval along with satisfying the manufacturing requirements and patient needs for a successful ophthalmic biomaterial.

4:20pm **AS+TF-TuA7 Surface Properties and Interfacial Bonding of Anodic Aluminium Oxides and Organic Resins**, Shoshan Abrahami, T. Hauffman, Vrije Universiteit Brussel (VUB), Belgium, De KoK, Fokker Aerostructures BV, Papendrecht, The Netherlands, Gulla, Ambat, Technical University of Denmark (DTU), Denmark, J.M.C. Mol, TU Delft, Netherlands, H. Terryn, Vrije Universiteit Brussel, Belgium

Aluminium pretreatment for bonding purposes needs to produce a stable oxide with optimal chemical and structural characteristics for adhesion with the organic resin. Contributions at the interface region can be related to adsorptive interactions as well as mechanical interlocking between the two phases. To separate between these two effects, we applied either barrier-type or porous-type oxides on two sets of specimens. This paper presents an overview of a study on the relation between oxide properties and interfacial bonding, as affected by the nature of electrolyte and the anodizing conditions, as well as changes in the chemistry of the organic resin (epoxy, phenol, silanes). A detailed characterization of different anodic oxides and its effect on the adsorption of resin-derived functional molecules was performed using X-ray photoelectron spectroscopy (XPS) and Fourier transform infrared spectroscopy (FTIR). Results indicate significant changes in the chemical composition of the oxides as a function of the electrolyte¹. Mechanical peel test performance indicate that the initial bond strength is independent of the oxide surface chemistry, while the stability under the ingress of water is correlated to the amount of surface hydroxyls². The presence of phosphates and sulphates did not alter bonding mechanisms, only the availability of hydroxyls. Further, scanning electron microscopy (SEM) and transmission electron microscopy (TEM) are used to characterize the geometrical modifications to the pore- and oxide structure in porous-type oxides. In addition, energy-dispersive X-ray spectroscopy (EDS) profiles were acquired on TEM cross-sections to assess the oxide structure and concentration of

resin inside the pores. Linking these morphological features to peel results show that two types of modifications are crucial for the formation of a strong and durable bonding³. A minimum pore size is needed for the resin to fill the oxide pores for good initial adhesion. Surface roughness, on the other hand, was found beneficial for the durability of the bond upon the ingress of water. Overall, the results demonstrate that both surface chemistry and oxide morphology contribute to the strength and durability of an adhesive bond.

1. Abrahami, S. T., et al., XPS Analysis of the Surface Chemistry and Interfacial Bonding of Barrier-Type Cr(Vi)-Free Anodic Oxides. *J. Phys. Chem. C* 2015, 119, 19967-19975.

2. Abrahami, S. T., et al., Effect of Anodic Aluminum Oxide Chemistry on Adhesive Bonding of Epoxy. *J. Phys. Chem. C* 2016, 120, 19670-19677.

3. Abrahami, S. T., et al., Interface Strength and Degradation of Adhesively Bonded Porous Aluminum Oxides *npj Materials Degradation* 2017, in press.

4:40pm AS+TF-TuA8 Practical Considerations of Different Ion Sources for Industrial Applications: The Good, the Bad, and the Indifferent, William Stickle, C.N. Young, M.D. Johnson, HP Inc., B. Schmidt, Physical Electronics USA

In recent years advances in ion gun technology have resulted in the routine application of cluster ion sources for analyses in industrial R&D labs. Most industrial laboratories study a wide variety of material systems ranging from polymers to inorganic thin films; many of these material systems require analysis not just of the as received surface, but also of and through the depth of a thin film. The purpose of this talk is to compare and contrast the benefits and drawbacks of performing routine XPS analyses using a mono atomic argon ion source compared with a C_{60}^+ ion source and an argon gas cluster ion source. From a practical standpoint, it is important to understand the sputter induced chemistry that may be created by these various sources and the trade-offs for applying these different primary ion sources for routine surface chemical analyses. The effects of preferential sputtering and chemical changes or reactions of metal oxides will be discussed. Several different material systems are examined and discussed by comparing the information obtained using mono atomic argon, an argon gas cluster source and a C_{60}^+ ion source for enhancing and clarifying 'routine' analyses. The different types of samples to be discussed will include polymers, fluoropolymer systems, amorphous metals and their oxides and multilayer thin films.

5:00pm AS+TF-TuA9 Surface Analysis in an Industrial Setting: Non-ideal Real World Samples, Vincent Smentkowski, General Electric Global Research Center

INVITED

The top few nanometers of a sample is defined as the surface. The surface is where most chemical reactions take place. There are many instances where the surface of materials are designed/functionalized in order to optimize properties and improve device performance; there are other instances where the surface becomes compromised and the material/device performance degrades following treatment and/or use. Accurate characterization is essential in order to understand material/device performance.

Auger Electron Spectroscopy (AES), X-ray Photoelectron Spectroscopy (XPS), Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and Scanning Probe Microscopy (SPM) are the most common, and commercially available, surface analysis techniques. These techniques provide complimentary information regarding both the composition and microstructure of the surface of a sample and often compliments bulk analysis.

In my talk, I will discuss the characterization challenges faced in an industrial setting where the surface analyst is often provided non-ideal samples and is asked to provide both a rapid and complete analysis of the sample. The criticality of talking with the person that submits the sample to understand their issue(s) and what they expect from the analysis (as well as being certain they realize possible complications) will be highlighted via real samples. I will also show a few examples where proof of principle results provided interesting data, however the data were not scientifically meaningful.

5:40pm AS+TF-TuA11 C 1s Peak of Adventitious Carbon Aligns to the Vacuum Level: Dire Consequences for Material's Bonding Assignment by Photoelectron Spectroscopy, Grzegorz Greczynski, L. Hultman, Linköping University, Sweden

X-ray photoelectron spectroscopy (XPS) is an irreplaceable analytical tool in materials research providing information about surface chemistry and composition. The unambiguous bonding assignment relies, however, on the correct measurement of binding energy (BE) values, which is often a nontrivial task due to the lack of an internal BE reference. C 1s signal from ubiquitous carbon contamination on samples forming during air exposure, so called adventitious carbon (AdC) layers, is the most common BE reference in XPS studies. Our literature review shows that in 58% of the top-cited papers dealing with XPS studies of magnetron sputtered films published between 2010 and 2016 in peer-reviewed journals, C 1s of AdC was used as

a BE reference, while, alarmingly, the remaining papers lack information about any referencing method used. Within the first group, C 1s peak was set quite arbitrary at the BE varying from 284.0 to 285.2 eV. This serious inconsistency contradicts the very notion of a BE reference, which per definition should be connected with one single-energy value.

In this work, we examine the reliability of using AdC for XPS BE referencing by measuring the position of C 1s peak for a series of transition metal (TM) nitride thin film layers that exhibit a well-defined Fermi edge cut-off serving as an internal BE reference. Measurements are performed as a function of the AdC layer thickness, which scales with the air exposure time. We show that the BE of C 1s peak E_B^F varies by as much as 1.44 eV, depending on the underlying (TM)N.[i] This is a factor of ten more than the typical resolvable difference between two chemical states of the same element, which makes BE referencing against the C 1s peak unreliable and thus inadvisable for the purpose. Surprisingly and reassuringly, we find that C 1s shifts correlate to changes in sample work function Φ_{SA} , such that the sum $E_B^F + \Phi_{SA}$ is constant at 289.50 ± 0.15 eV, irrespective of materials system and air exposure time, indicating vacuum level alignment. This discovery allows for significantly better accuracy of chemical state determination through a complementary measurement of Φ_{SA} and referencing to C 1s set at $289.50 - \Phi_{SA}$, which as we demonstrate, yields consistent results for the whole series of TM nitrides, irrespective of air exposure time. Our findings are not specific to nitrides and likely apply to all systems where charge transfer at the AdC/substrate interface is negligible.

[i] G. Greczynski and L. Hultman, *ChemPhysChem* 18 (2017) 1507

6:00pm AS+TF-TuA12 Band Energy Alignment Studies at Heterojunction by X-ray Photoelectron Spectroscopy (XPS), Jisheng Pan, Institute of Materials Research and Engineering, A*STAR (Agency for Science, Technology and Research), Singapore

The performance of any type of hetero-junction device is determined by two kinds of interface parameters: the band discontinuities and the built-in potential. Therefore, determining heterojunction band offsets and tuning them to a desired application would have an obvious impact on the optimization of the devices. Many techniques have been developed to determine the interfaces and to understand the microscopic origin of the interface properties. XPS is more widely used technique to study band alignment of heterojunction, probably due to its capability to simultaneously detect interface chemical and electronic properties which can be exploited for fully understanding of distinct correlations between the thin film material characteristics and device performance. There are two ways to obtain energy band offsets using XPS. One is direct measurement of valence band spectrum from interface, and this spectrum is simply considered as a superposition of substrate-related and overlayer-related valence band spectra. A nonlinear least squares fit is performed to separate it to substrate-related and overlayer-related valence band spectra to determine two valence band maxima and, valence band offset (VBO) of interface. The conduction-band offset CBO is deduced from VBO and suitable reference gap values of two materials at interface. It can be seen that the accuracy of the band offsets determined through this way depends on the fitting procedure. In order to overcome the above problem and obtain reliable band offset data, a method was proposed to determine band offsets by combination of core level and valence band spectra. No fitting procedure is involved in this method. However, accurate XPS determination of band alignment in this way requires careful consideration of many other possible effects. In this paper, we have studied the effects of chemical shift, differential charging, band bending and photoemission final state on the determination of heterojunction band offsets using Kraut's method. The method has also been applied to determine energy-band alignments of molybdenum disulphide (MoS_2) monolayer on high-k dielectric oxides such as Al_2O_3 and ZrO_2 . The VBO on monolayer MoS_2/Al_2O_3 (ZrO_2) interface was measured to be 3.31 eV (2.76 eV), while the CBO was 3.56 eV (1.22 eV). For bulk MoS_2/Al_2O_3 interface, both VBO and CBO increase by 0.3 eV, due to the upwards shift of $Mo\ 4d_{z^2}$ band. The symmetric change of VBO and CBO implies Fermi level pinning by interfacial states. Our finding ensures the practical application of both p-type and n-type MoS_2 based complementary metal-oxide semiconductor and other transistor devices using Al_2O_3 and ZrO_2 as gate materials.

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