Wednesday Afternoon, October 24, 2018

Applied Surface Science Division
Room 204 - Session AS+SE-WeA

Industrial and Practical Applications of Surface Analysis

Moderators: Jeffrey Fenton, Medtronic, Inc., Svitlana Pylypenko, Colorado School of Mines

2:20pm AS+SE-WeA-1 Identification of Unknown Contaminants in Industrial Applications Using MS/MS in Combination with High Resolution Mass Spectrometry, *A Pirkl, **Julia Zakel**, D Rading,* IONTOF GmbH, Germany*; N Havercroft,* IONTOF USA*; S Kayser, H Arlinghaus, R Moellers, E Niehuis,* IONTOF GmbH, Germany

The fast and reliable characterisation of unknown contaminants in quality control procedures is crucial in many industrial areas to understand manufacturing errors and avoid production downtime. TOF-SIMS nowadays plays an important role in this area especially due to its fast imaging capabilities that enable the acquisition of chemical surface images with a lateral resolution in the 100 nm range.

However, molecular identification of unknown substances can be hampered by constraints in mass resolution and mass accuracy of a standard TOF analyser. To overcome this problem, we have developed a new Hybrid SIMS instrument, which uniquely combines all advantages of a state-of-the-art TOF-SIMS with the mass spectrometry performance of an Orbitrap mass analyzer (Q Exactive™ HF) [1]. The Q Exactivemass spectrometer provides a mass resolution of more than 240,000 @ m/z = 200, sub ppm mass accuracy, and fully integrated MS/MS capabilities that allow low energy collision induced fragmentation for structural analysis of complex molecules. All in all this dramatically increases the level of confidence for the SIMS analysis.

Different applications ranging from polymers to metals will be presented with a focus on the identification of unknown substances by MS/MS in combination with high resolution mass spectrometry. Furthermore dedicated measurement modes and strategies that can be applied to different forms of contaminants will be presented. The use of databases will be showcased which further assists and confirms the results of a manual data evaluation.

[1] The 3D OrbiSIMS – Label-Free Metabolic Imaging with Sub-cellular Lateral Resolution and High Mass Resolving Power, Passarelli et al., Nature Methods, 2017, 14(12):1175-1183, DOI 10.1038/nmeth.4504.

2:40pm AS+SE-WeA-2 ToF-SIMS Analysis of Glass and Glass Coatings, *Christine Mahoney,* Corning Inc.

Many think of glass as being an inert material. However, glass contains many reactive alkalis and other elements that can interact and diffuse into solutions or into coatings. These alkalis tend to decrease the chemical durability of the glass itself, and can play a key role in accelerating corrosion and delamination mechanisms involving the glass. How we manufacture and process the glass plays a significant role in its chemical durability and reactivity. The reactivity of a glass surface can be particularly problematic for pharmaceutical applications, where glass delamination in vials and/or drug interactions with glass constituents can potentially occur. Here we present an overview of ToF-SIMS research at Corning involving the analysis of glass surfaces and their associated coatings. Both organic and inorganic applications will be discussed, using a wide range of tools for analysis.

3:00pm AS+SE-WeA-3 Problem Solving with Valence Band Spectroscopy and SIMS MS/MS, *Steven Pachuta, D Poirier,* 3M Company   **INVITED**

Surface chemistry is often key to the performance of materials like films, coatings, and adhesives. Controlling and understanding surface chemistry is therefore critical to manufacturers. X-ray photoelectron spectroscopy (XPS) is the workhorse in industrial surface characterization laboratories, followed closely by time-of-flight secondary ion mass spectrometry (ToF-SIMS). XPS survey spectra provide quantitative elemental information on surfaces, and XPS high energy-resolution spectra can give information on chemical states. ToF-SIMS, in general, gives even more specific surface chemical information, such as the identities of polymer additives and surface contaminants.

This presentation will describe efforts to increase the chemical specificity of both XPS and ToF-SIMS for organic species, especially polymers. The XPS valence band region contains a complex fingerprint which is highly dependent on molecular structure. By using databases in combination with multivariate methods such as principal component analysis (PCA) and

partial least squares (PLS), a surprising degree of information can be extracted from valence band spectra of unknown materials.

The fact that many real-world surfaces comprise a mixture of components is a recurrent frustration in industrial surface characterization. ToF-SIMS analysts have long envied their GC/MS and LC/MS counterparts, who have the luxury of separating mixtures before doing mass spectrometry. The recent commercial availability of tandem mass spectrometry (MS/MS) on ToF-SIMS instruments has gone some way towards addressing the mixture problem and has increased the ability of ToF-SIMS to identify unknown materials. Examples will be presented.

4:20pm AS+SE-WeA-7 Surface and In-depth XPS Characterization of Liquid and Cured Control Release Additives (CRAs) Used in Silicone-Based Release Coatings, *Brian Strohmeier, K Rhodes, R Munigeti, J Orlowski,* Avery Dennison Corporation

Silicone-based release coatings are used in a wide variety of commercial applications including: release liners for removable pressure sensitive adhesive laminates and tapes, release papers and polymer films, non-stick packaging, and other products where a specific force of peel separation is required between two different film materials during processing or storage. Typical industrial silicone-based release coatings consist of UV or heat cured mixtures of silicone compounds and controlled release additives (CRAs). CRAs commonly contain proprietary mixtures of functionalized silanes, siloxanes, and silica, plus a variety of other organic components. The release properties of silicone-based release coatings depend highly on the distinct types and relative amounts of the silicone compounds and CRAs used in the cured mixture. Therefore, it is of great interest to quantitatively characterize the silicone and CRA components on the surface of silicone release coatings for improved product and process development as well as problem-solving related to release issues. In this study, a variety of commercial CRA products were characterized by gel permeation chromatography (GPC) for bulk molecular weight distribution information and by X-ray photoelectron spectroscopy (XPS) for surface composition and chemistry. The CRA materials studied had vapor pressures that allowed successful XPS characterization in the liquid state. Surprisingly, the CRA liquids could even be sputtered and/or depth profiled using argon cluster ions, whereas sputtering with monatomic argon ions resulted in XPS chemical state changes caused by ion beam induced sample damage. The CRA materials were characterized by XPS and argon cluster ion sputtering/depth profiling in the pure liquid state and in solid heat cured release coating mixtures with polydimethyl siloxane (PDMS). The high resolution Si 2p XPS spectra obtained for cured silicone release coatings of known composition could be peak-fitted into separate CRA and PDMS components to produce a quantitative calibration curve for evaluating release coatings with unknown CRA/silicone compositions.

4:40pm AS+SE-WeA-8 Differentiating Silicones Using SIMS, *Paul Vlasak, M Pacholski,* The Dow Chemical Company

The unique properties of poly(dimethylsiloxane), also known as PDMS or silicone, have allowed PDMS-based materials to proliferate in modern industry. A huge variety of applications using PDMS have been developed including structural adhesives, release agents, optical components, lubricants, anti-foam agents, and potting agents to name a few.

Considering the omnipresence of PDMS in industrial settings along with its low surface energy and tendency to migrate, it comes as no surprise that PDMS is frequently encountered in industrial surface analysis laboratories. Because PDMS is readily detected and easily recognized by its characteristic fragmentation pattern, SIMS is well suited to identifying the presence of silicones on a wide range of materials.

In some instances, the analyst expects to find PDMS on a sample surface. For example, the PDMS transferred from a silicone release liner onto an adhesive may be of interest. In other instances, PDMS can be encountered as an unexpected contaminant, perhaps interfering with adhesion or causing defects in a coating or painting operation. In either case, besides its mere presence, the structural details of the PDMS may be important to understanding the behavior of the adhesive/release system or discovering the actual source of a contaminant amongst multiple possibilities.

From a pragmatic standpoint, the current work explores how molecular weight, endgroup type, and other structural factors influence PDMS fragmentation patterns through the use of well-characterized reference materials. The effects of instrument-related parameters as well as film thickness and substrate type will also be considered to the extent these factors influence the spectra obtained.

Wednesday Afternoon, October 24, 2018

5:00pm AS+SE-WeA-9 Uranium Particles Analysis and Imaging Using ToF-SIMS for Source Identification, *Juan Yao*, E Krogstad, S Shen, Z Zhu, X Yu, Pacific Northwest National Laboratory

Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a highly surface sensitive analytical tool. It offers excellent limits of detection (LODs) of part per million with sub-micron spatial resolution. Besides determining isotopic ratios of radioactive materials, ToF-SIMS has the advantage of providing full mass spectra with m/z up to 2000 Da, allowing the detection of chemical signatures in a material. This latter feature is very attractive to identify the source of uranium and other radioactive materials in single particles. We analyzed three different NIST standard reference materials with varied concentrations of uranium in this study. Samples are in the form of glass wafers and particles deposited on a substrate. By applying spectral principal component analysis (PCA), the SIMS mass spectra obtained from the same type of NIST sample show consistent features; regardless of the sample form. Furthermore, a blind test was conducted using a mixture consisting of particles from all three NIST materials. Our spectral PCA results illustrate that ToF-SIMS can be a useful tool to differentiate particles of different origins and potentially applicable for signature identification in single particles. In addition, scanning electron microscopy (SEM) was applied to complement the SIMS imaging for correlative analysis [1]. It is beneficial to use SEM to obtain particle morphological information. However, SEM lacks the sensitivity in single particle elemental analysis compared to ToF-SIMS. Our work demonstrates that ToF-SIMS is a powerful tool for analysis of individual radioactive particles to fulfill nuclear safeguards and forensic missions.

5:20pm AS+SE-WeA-10 XPS Depth Profiling of Organic Resins with Inorganic Inclusions, *Benjamin Schmidt*, J Newman, J Mann, L Swartz, Physical Electronics

Many industrial materials are derived from plastics due to low cost and ease of manufacturing, and they may also include additives such as TiO_2 or SiO_2 to provide desirable mechanical, thermal, and other properties. Surface analysis techniques such as XPS are quite useful for characterizing the chemistry of these composite materials, but it can be difficult to perform reliable sputter depth profiling due to different rates and behaviors of organic and inorganic components under ion beam bombardment. For example, monoatomic argon ion sputtering is well-known to damage polymer layers and also cause chemical reduction in transition metal oxides such as TiO_2. The development of cluster ion beams has expanded the capabilities of profiling, but mixed organic/inorganic composites still present challenges. Preliminary results have shown that in the presence of an organic matrix, chemical reduction of metal oxide additives can lead to observed carbide species, which may not be representative of the bulk material.

In this work, we compare the effects of using different ion beams for XPS depth profiling inorganic-filled epoxy resins. Several ion beams were used for profiling, including monoatomic argon, C_{60} gas cluster, and argon gas cluster. We investigate stoichiometry, chemical bonding environment, and surface morphology to provide suggested depth profiling conditions for these organic/inorganic composites.

5:40pm AS+SE-WeA-11 Application of X-ray Photoelectron Spectroscopy to Degradation Studies of Electrodes in Fuel Cells and Electrolyzers, *Kateryna Artyushkova,* University of New Mexico; *N Danilovic,* Lawrence Berkeley Lab, University of California, Berkeley; *C Capuano,* Proton on site; *A Serov,* Pajarito Powder LLC; *P Atanassov,* University of New Mexico

The stability of materials used used in anodes and cathodes in fuel cells and electrolyzers is a critical factor for practical industrial applications. To improve the longevity, it is important to link the chemical structure to degradation mechanisms and changes in the surface composition of the catalyst on the electrodes. Application of x-ray photoelectron spectroscopy (XPS) to probe structure of catalytic materials and their degradation is becoming an important analytical approach due to its accessibility and quantitative chemical information provided. This talk will present several examples of application of high-resolution XPS for analysis of the chemistry of electrodes and changes that are occurring during operation in several technological platforms, such as proton-exchange membrane fuel cells (PEMFCs), alkaline membrane fuel cells (AEMFC), direct methanol fuel cells (DMFC), direct hydrazine fuel cells (DHFC) and water electrolyzers (WE).

6:00pm AS+SE-WeA-12 Application of X-ray Photoelectron Spectroscopy in Semiconductor Industry, *Yibin Zhang*, Z Bayindir, Z Sun, M Zhu, J Gao, X Wang, T Han, J Shu, D Shao, J Riendeau, J Liu, GLOBALFOUNDRIES

Over several decades, X-ray Photoelectron Spectroscopy (XPS) has been widely used for surface issues in chemistry-based industries. It was limited in its application for semiconductors due to film thickness and chemical change of material during the Ar+ sputtering process. Over the past ~15 years, things have slowly changed as the semiconductor industry has evolved. There has been a steady decrease in the thickness of many layers of the "thin film" structure down to the sub nanometer. This has made XPS a highly suitable technique for material characterization of the whole film, because of the correlation in film thickness to XPS probing depth (~10nm). In addition, surface and interfacial layers on the nanometer scale were technologically irrelevant when thin thickness approached micrometer (μm) dimension. Today, as films go down to a few nanometers; the interface reaction might consume a considerable fraction of overall film thickness and strongly affect many film properties. In this presentation, several case studies in semiconductor industries will be investigated, like High K materials – HfO_2, SiN_xO_y, ultra-low K materials, metal gate material (TiN and TiAlN) work function control, and contamination analysis on small pads on patterned wafers. Opportunities and challenge for XPS application in the semiconductor world will be discussed.

Author Index

Bold page numbers indicate presenter

— A —
Arlinghaus, H: AS+SE-WeA-1, 1
Artyushkova, K: AS+SE-WeA-11, **2**
Atanassov, P: AS+SE-WeA-11, 2
— B —
Bayindir, Z: AS+SE-WeA-12, 2
— C —
Capuano, C: AS+SE-WeA-11, 2
— D —
Danilovic, N: AS+SE-WeA-11, 2
— G —
Gao, J: AS+SE-WeA-12, 2
— H —
Han, T: AS+SE-WeA-12, 2
Havercroft, N: AS+SE-WeA-1, 1
— K —
Kayser, S: AS+SE-WeA-1, 1
Krogstad, E: AS+SE-WeA-9, 2
— L —
Liu, J: AS+SE-WeA-12, 2

— M —
Mahoney, C: AS+SE-WeA-2, **1**
Mann, J: AS+SE-WeA-10, 2
Moellers, R: AS+SE-WeA-1, 1
Munigeti, R: AS+SE-WeA-7, 1
— N —
Newman, J: AS+SE-WeA-10, 2
Niehuis, E: AS+SE-WeA-1, 1
— O —
Orlowski, J: AS+SE-WeA-7, 1
— P —
Pacholski, M: AS+SE-WeA-8, 1
Pachuta, S: AS+SE-WeA-3, **1**
Pirkl, A: AS+SE-WeA-1, 1
Poirier, D: AS+SE-WeA-3, 1
— R —
Rading, D: AS+SE-WeA-1, 1
Rhodes, K: AS+SE-WeA-7, 1
Riendeau, J: AS+SE-WeA-12, 2
— S —
Schmidt, B: AS+SE-WeA-10, **2**

Serov, A: AS+SE-WeA-11, 2
Shao, D: AS+SE-WeA-12, 2
Shen, S: AS+SE-WeA-9, 2
Shu, J: AS+SE-WeA-12, 2
Strohmeier, B: AS+SE-WeA-7, **1**
Sun, Z: AS+SE-WeA-12, 2
Swartz, L: AS+SE-WeA-10, 2
— V —
Vlasak, P: AS+SE-WeA-8, **1**
— W —
Wang, X: AS+SE-WeA-12, 2
— Y —
Yao, J: AS+SE-WeA-9, **2**
Yu, X: AS+SE-WeA-9, 2
— Z —
Zakel, J: AS+SE-WeA-1, **1**
Zhang, Y: AS+SE-WeA-12, **2**
Zhu, M: AS+SE-WeA-12, 2
Zhu, Z: AS+SE-WeA-9, 2