

Thursday Afternoon, November 2, 2017

Applied Surface Science Division

Room: 13 - Session AS+SS-ThA

Advances in Instrumentation and Data Analysis

Moderators: Thomas Grehl, ION-TOF GmbH, Germany,
Bonnie June Tyler, Universität Münster

2:20pm **AS+SS-ThA1 Submicron Spot Sampling Resolution in Thermal Desorption Atomic Force Microscopy - Mass Spectrometry Via Rapid Heating Functions**, *S. Somnath, S. Jesse, Gary Van Berkel, S.V. Kalinin, O.S. Ovchinnikova*, Oak Ridge National Laboratory

Atomic Force Microscopy (AFM) combined with Mass Spectrometry (MS) can provide the ability to map and correlate the molecular and physical properties of samples at sub-micron resolutions. One such hybrid system employs heated AFM probe for thermal desorption (TD) sampling of molecules from a surface and subsequent gas phase ionization and detection of the liberated species by MS. However, current heating techniques typically result in a minimum spot size of 1-2 μm for most real-world samples where the where the melting and vaporization points are further apart since the majority of the thermal energy from the thermal probe only melts or damages the substrate. While substantial research in the past has focused on improving the instrumentation, the waveforms used for heating thermal probes have been ignored. Heated AFM probes are capable self-heating at rates approaching $1\text{E}+9$ K/s to reach temperatures in excess of 1300 K. Prior research has shown that increasing the heating rate ($> 1\text{E}+9$ K/s) can enable thermal desorption of intact molecules off the sample surface.

Here, we report on the use of voltage pulse trains to tailor probe heating such that spot sampling size was reduced and desorption efficiency (DE), defined as the ratio of the mass spectral signal to the volume of the desorption crater, was improved compared to the conventional heating method. We developed a 1D finite element joule-heating model of the probe-sample system that predicted the cantilever response to different heating functions, to guide the development and optimization of the heating functions and aid in interpreting experimental results. Using a model system composed of a thin film of ink containing pigment yellow 74 as a model system, desorption craters shrunk from 2 μm , using the conventional approach, to 310 nm using the optimum tailored heating function. This same pulsed heating function produced a $381\times$ improvement in the DE and an $8\times$ improvement in spatial resolution compared to the conventional heating approach showing that signal/amount of material sampled was improved significantly by this new probe heating strategy.

3:00pm **AS+SS-ThA3 Data Analysis in Thin Film Characterization: Learning More With Physical Models**, *Lev Gelb, A.V. Walker*, University of Texas at Dallas **INVITED**

Chemical imaging methods, including imaging mass spectrometry (MS), are increasingly used for the analysis of samples ranging from biological tissues to electronic devices. Most chemical analyses for advanced materials, nanosystems, and thin films involve energetic beams of primary ions or electrons. These unavoidably cause chemical damage, including surface roughening, which confuses data interpretation. In secondary ion mass spectrometry (SIMS) matrix effects can be significant, in which the signal obtained from a given species may change depending on its surroundings. All these phenomena lead to the same issue: the data measured are not necessarily representative of the elements or species originally present, or their original locations. These effects can sometimes be exploited to provide new information or increased sensitivity, as in matrix-enhanced SIMS and the determination of overlayer thicknesses from attenuation of XPS substrate intensity.

We discuss analysis of such data using maximum *a posteriori* (MAP) reconstruction based on physically motivated models, and contrast this approach with statistical dimensionality-reduction techniques such as Principal Components Analysis. We present progress towards the quantitative extraction of chemical concentration profiles, component spectra, sample topography and other information from imaging mass spectrometry data in the presence of matrix effects. These include systems that demonstrate "weak" matrix effects, such as mixed self-assembled monolayers, and "strong" matrix effects such as those observed in ionic liquid matrix enhanced secondary ion mass spectrometry.

We also draw comparisons with related nonlinearities in other analysis methods, in particular X-ray photoelectron spectroscopy (XPS). While XPS is often considered to have linear response with concentration, this is only true under certain conditions and does not necessarily apply in sputter-based

depth profiling experiments. We discuss extension of the MAP approach to such experiments and point out similarities with its application to SIMS data.

4:00pm **AS+SS-ThA6 Advanced Analysis of XPS and ToF-SIMS Data**, *Matthew Linford, S. Chatterjee, B. Singh*, Brigham Young University, *N. Gallagher, Eigenvector Inc., M.H. Engelhard*, EMSL, Pacific Northwest National Laboratory **INVITED**

Surface analysis plays a critical role in many areas of science and industry, and X-ray photoelectron spectroscopy (XPS) and time-of-flight secondary ion mass spectrometry (ToF-SIMS) are much used analytical techniques that provide information about the outermost layers of materials. In this presentation, I discuss the application of multivariate spectral techniques, including principal component analysis (PCA) and multivariate curve resolution (MCR), to the analysis of XPS and ToF-SIMS depth profiles. Multivariate analyses often provide insight into data sets that is not easily obtained in a univariate fashion. The information content (IC) or entropy, which is based on Shannon's information theory, is also introduced. This approach is not the same as the mutual information/entropy approaches sometimes used in data processing. A discussion of the theory of each technique is presented. PCA, MCR, and IC are applied to four different data sets obtained via a ToF-SIMS depth profile through ca. 100 nm of C_3F_6 on Si, a ToF-SIMS depth profile through ca. 100 nm of PNIPAM (poly (N-isopropylacrylamide)) on Si, an XPS depth profile through a film of SiO_2 on Si, and an XPS depth profile through a film of Ta_2O_5 on Ta. PCA, MCR, and IC reveal the presence of interfaces in the films, and often indicate that the first few scans in the depth profiles are different from those that follow. Both IC and backward difference IC analysis provide this information in a straightforward fashion. Rises in the IC signal at interfaces suggest greater complexity to scans from interfaces in depth profiles. Results from PCA were often rather difficult to understand owing to the complexity of its scores and loadings plots. MCR analyses were generally more interpretable.

4:40pm **AS+SS-ThA8 Using the Auger D-Parameter to Identify Polyatomic Molecular Species**, *Sabrina Tardio, P.J. Cumpson*, NEXUS, Newcastle University, UK

When analysing organic materials using XPS, the interpretation of the C1s spectra can be quite challenging and particularly difficult is to distinguish between unsaturated/aromatic carbon (hybridised sp²) and aliphatic carbon (hybridised sp³). This is because their binding energies of the two are very close and, in some cases, overlap or even invert the expected trend. This problem can be approached by observing the CKLL auger peak of the XPS spectra that is present around 260 eV of kinetic energy. Historically, information on the C sp²/sp³ ratio is obtained by analysing the width of this, extracting a metric commonly known as the D-Parameter. This is calculated by taking the first derivative of the auger feature and measuring the distance (in eV) between the position of the maximum (the most positive) and the minimum (the most negative) peaks observable. It was shown that there is a linear correlation between the D-Parameter with sp² hybridised carbon content in a surface. For example, graphite (100% sp² character) has a D-Parameter around 22eV while diamond (100% sp³ character) has a D-Parameter around 13eV. The D-Parameter is widely used for the identification of carbon allotropes; graphite, graphene, amorphous, diamond like carbon (DLC) diamond, hydrogenated diamond etc. However, the metric has found little or no use for the identification of unsaturated and saturated carbon in polymers or, more generally, polyatomic molecules. Although the principle remains the same; the correlation between D-parameter and sp² carbon is still true, the presence of hydrogen as well as other atoms other than carbon, makes the relationship between the two much more complex. In this work correlations of the D-parameter with the C Sp²/sp³ ratio, the ratio between hydrogen bonded to C sp² and sp³ and the ratio between heteroatoms (such as oxygen) bonded to sp² and sp³ carbons is shown. In particular, a linear relationship between a combination of these ratios and the d-parameter was found. This allows one to predict the d-parameter for a given organic compound as well as to obtain more information about unknown species analysed. It will be shown how the combination of different information obtained from XPS spectra: photoelectron high-resolution peaks (C1s O1s), valence band and D-Parameter can lead to a quite accurate identification of organic molecules.

5:00pm **AS+SS-ThA9 XPS Analysis of Multilayer HfO₂ Using Hard and Soft X-rays**, *Jennifer Mann*, Physical Electronics, *R. Inoue, H. Yamazui, K. Watanabe*, ULVAC-PHI, Japan, *J. Newman*, Physical Electronics

Hard x-rays can generally be considered as having photon energies > 5 keV, while photon energies below 5 keV are described as soft x-rays. Hard x-ray photoelectron spectroscopy (HAXPS) is typically performed at large synchrotron facilities, while most commercial lab-scale XPS instruments use soft x-rays. The PHI *Quantes* is a new commercial laboratory instrument

equipped with two scanning microprobe, monochromated x-ray sources, Cr K α (5414.9 eV) and Al K α (1486.6 eV). Use of higher photon energies increases the mean free path of photoelectrons, resulting in an increased information depth obtained from the sample (~3x that of Al K α). HAXPS measurements are therefore more sensitive to the bulk and contributions from the surface are minimized [1,2]. Toggling between x-ray sources allows non-destructive depth analysis of multilayer thin films and buried interfaces [1]. A more detailed description of the instrument will be presented in reference [3].

Initial analysis results on the high-k dielectric, HfO $_2$, obtained on the PHI *Quantex* using both hard and soft x-ray sources will be presented. Several samples of HfO $_2$ on SiO $_2$ on Si substrate with varying thicknesses of the HfO $_2$ and SiO $_2$ layers were analyzed. The HfO $_2$ /SiO $_2$ thicknesses of the samples are as follows: 27Å/28Å, 80Å/22Å, 81Å/81Å and 263Å/22Å. Spectra were collected with a 90 degree take-off angle to maximize the information depth of each sample. As expected, the presence and relative intensities of SiO $_2$ and Si substrate peaks varied depending on the sample thickness, photon energy and photoelectron kinetic energy.

[1] Kobayashi, K. Hard X-ray photoemission spectroscopy, *Nucl. Instr. Meth. Phys. Res. A* **2009**, 601, 32-47.

[2] Fadley, C.S. Hard X-ray Photoemission: An Overview and Future Perspective. In *Hard X-ray Photoelectron Spectroscopy (HAXPS)*; Woicik, J. C., Ed; Springer: Switzerland 2016.

[3] Inoue, R., Yamazui, H., Watanabe, K., Newman, J., Mann, J. E., Design and Application of a New Laboratory HAXPES Instrument, ECASIA 2017.

5:20pm AS+SS-ThA10 Novel Systems Toward Ambient Pressure Photoemission Spectroscopy, *Lukasz Walczak*, PREVAC, Poland

Nowadays, the complexity of materials and their surfaces is expanded across a wide range of topics, including surface science, catalysis, corrosion, photoelectrochemical energy conversion, battery technology, or energy-saving technologies [1-6]. An unique and exceedingly flexible analysis cluster with a detection system is needed for this applied research. Here the examples of innovative, compact ambient pressure X-ray spectroscopy systems with some experimental results. One of the examples will be a laboratory based high pressure x-ray photoelectron spectroscopy (HPXPS). The focus is on the usability of the system for various types of studies relevant for high level research for photo-catalytic reactions, light harvesting and solar cell development [6]. Further examples will be the advanced HP cell with the ambient pressure X ray spectroscopy system and flexible gas inlet system to allow for frontier research on gas-solid interactions. Systems are equipped with the possibility of process automatization in different environments. Additionally it will be presented a spectrometer for the ambient pressure photoemission spectroscopy with a new monochromatic source, in order to permit complete characterization of the energy, angular, and later resolutions using different metal samples at different pressures.

References

S. Bengió, et al. *Surf. Sci.* 646, 126 - 131 (2016)

B. Eren et al. *Science* 29, 475-478 (2016)

Z. Duan et al. *J. of Solid St. Electrochem.* 19, 2265 - 2273 (2015)

K. Samson et al. *ACS Catalysis*, 4, 373 - 374 (2014)

Yi-Chun Lu et al. *Sci. Rep.* 2, 715 (2012)

C. S. Gopinath et al. *ChemCatChem* 7, 588 – 594 (2015)

5:40pm AS+SS-ThA11 Fabrication and Characterization of Heusler-Based Fe-Mn-Ge Epitaxial Films, *B.D. Clark, N. Naghibolashrafi, S. Gupta, J. Jones, P.R. LeClair, A. Gupta, Gary Mankey*, University of Alabama

Half metallic alloys have a wide range of applications such as spin filters, spin polarizers, and high signal giant magnetoresistive devices. The Heusler family of alloys is predicted to have a large number of half-metallic alloys. The MINT Center at UA maintains an extensive database of Heusler alloys (<http://heusleralloys.mint.ua.edu/>) to track and contribute to the application of Heuslers in technology applications. The formation of stable crystal structures that match theoretical predictions is one issue that we are addressing experimentally. In this work, high temperature magnetron sputtering is applied in an attempt to stabilize predicted phases. The sputtering system is confocal with four targets, so alloy composition can be controlled by carefully adjusting the power to separate magnetron guns containing elemental targets of Fe, Mn, and Ge. Both in-situ and ex-situ techniques are applied to evaluate the resulting films. For in-situ flux monitoring, a quartz crystal microbalance is used; for in-situ chemical analysis, Auger electron spectroscopy with a cylindrical mirror analyzer is performed; and for in-situ structural analysis, reflection high-energy electron diffraction is performed. The ex-situ techniques employed include x-ray reflectivity and diffraction, scanning transmission microscopy with selected area diffraction, energy dispersive x-ray analysis, and variable temperature

magnetometry and transport. Our characterization results show that when deposited on sapphire, the full-Heusler Fe $_2$ MnGe forms in the hexagonal DO $_19$ crystal structure instead of the predicted L2 $_1$ phase. The equiatomic half-Heusler alloy of FeMnGe forms in the C1 $_b$ crystal structure when deposited on MgO(100). The results underline the importance of complete complimentary characterization techniques that include both chemical and structural analysis since the principle x-ray diffraction peaks of the L2 $_1$ and C1 $_b$ structures occur at the same locations. The two types of alloy films that were fabricated also exhibit markedly different magnetic behavior which will be discussed in detail.

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