

Tuesday Afternoon, October 26, 2021

Live Session

Room Live-2 - Session LI-TuA2

Tuesday Afternoon Live Session II: Novel Characterization and Modeling

Moderators: Mohan Sankaran, University of Illinois at Urbana-Champaign, Virginia Wheeler, U.S. Naval Research Laboratory

12:50pm **LI-TuA2-1 Welcome and Opening Remarks, Ginger Wheeler, U.S. Naval Research Laboratory**

Welcome to the AVS 67 Virtual Symposium! We hope you will enjoy the event!

12:55pm **LI-TuA2-2 Time-Resolved Photoelectron Spectroscopy of Solar Cell Materials, Ute Cappel, KTH - Royal Institute of Technology, Sweden**
INVITED

Solar cells have a great potential in replacing fossil fuels in electricity generation, if requirements of low production costs can be met. In the last years, much research has focused on developing new solar cells made from organic or hybrid materials, which can be fabricated by cheap methods. This includes solar cells with a hybrid organic inorganic perovskite as the active layer in the solar cell, which have now reached power conversion efficiencies of more than 25%. In a typical solar cell, the perovskite layer is sandwiched between two selective contacts, one for holes and one for electrons.

The future success of these developments crucially depends on understanding the details charge separation, charge transport and charge recombination at the interfaces between the different layers in a solar cell as well as what parameters limit solar cell stability. X-ray based techniques such as photoelectron spectroscopy (PES) are powerful tools for obtaining electronic structure information of materials at an atomic level. By varying the photon energy from soft to hard X-rays, photoelectron spectroscopy can be used for non-destructive depth profiling of the solar cell interfaces giving information about the energy alignment and chemical structure and composition at the interface.

In this presentation, I will describe how we have used photoelectron spectroscopy for time-resolved and *operando* studies of complete solar cells. I will present results, where we were able to measure PES of a complete perovskite solar cells while applying an external bias and during visible illumination. This allowed us to determine the electronic structure and energy alignment of the active layer / back contact interface of the solar cell under operating conditions. Furthermore, I will discuss how time-resolved pump-probe measurements can be used to determine electron transfer dynamics in solar cells. For this, I will give an example of measuring the electron transport times in lead sulfide quantum dots films by combining photoelectron spectroscopy with sample excitation by a visible short-pulsed laser [1]. The described methods provide new ways of gaining insights into the working mechanism of solar cells based different combinations of materials.

[1] T. Sloboda et al. Scientific Reports, 10, 1-14 (2020).

1:15pm **LI-TuA2-6 Application of a Laboratory-Based Scanning XPS/HAXPES Instrument for the Characterization of Buried Interfaces, Kateryna Artushkova, J. Mann, J. Newman, Physical Electronics USA; R. Inoue, K. Watanabe, H. Yamazui, ULVAC-PHI, Inc., Japan; A. Vanleenhove, C. Zborowski, T. Conard, IMEC, Belgium**
INVITED

X-ray Photoelectron Spectroscopy (XPS) is a widely used surface analysis technique with many well established industrial and research applications. The surface sensitivity (top 5-10 nm) of XPS and its ability to provide short-range chemical bonding information make the technique extremely popular in materials characterization and failure analysis laboratories. While its surface sensitivity is an important attribute, in some cases, the depth of analysis of XPS is not sufficient to analyze buried interfaces without first sputter etching the sample surface. However, sputter etching can often lead to alterations of the true surface chemistry. An alternative to sputter etching the sample is Hard X-ray Photoelectron Spectroscopy (HAXPES), available at some synchrotron facilities. HAXPES utilizes X-rays typically defined as having energies greater than 5 keV. By increasing the photon energy of the X-ray source, the mean free path of photoelectrons is increased, resulting in an increased information depth obtained from the sample. Depending on the energy used, these hard X-rays can provide depths of analysis three or more times than that of soft x-rays used on conventional XPS systems. HAXPES measurements are, therefore, more

sensitive to the bulk, and contributions from the surface are minimized.^{1,2} This presentation will describe a laboratory-based instrument, the PHI *Quantes*, equipped with two scanning microprobe monochromated X-ray sources, Al K α (1486.6 eV) and Cr K α (5414.7 eV), thus enabling both traditional XPS and HAXPES experiments in the same instrument. By combining both soft and hard X-ray analyses, we can gain an even better understanding of composition with depth and information at buried interfaces.

References

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.

1:35pm **LI-TuA2-10 Precise Ion Energy Control With Tailored Waveform Biasing: Determination of Sputter Thresholds as Input for ALE Process Design, Nicholas Chittock, S. Balasubramanyam, T. Faraz, Y. Verstappen, Eindhoven University of Technology, Netherlands; M. Verheijen, Eurofins Materials Science, Netherlands; J. Escandon-Lopez, E. Heijdra, W. van Gennip, Prodrive Technologies, Netherlands; E. Kessels, A. Mackus, Eindhoven University of Technology, Netherlands**
INVITED

Anisotropic atomic layer etching (ALE) relies on the use of directional ions having an energy within a specific ion energy window to remove a modified surface layer.¹ The selectivity and etch control of ALE depend strongly on the ability to limit the ion energy within this window. However, tuning of the ion energy is often achieved by application of a radio-frequency sinusoidal bias voltage waveform to the substrate, which results in a relatively broad ion energy distribution leading to a loss of selectivity.² In this work, we report on employing tailored waveform bias voltages to accurately control the ion energy during ALE.

A prototype bias voltage generator from Prodrive Technologies was used to produce tailored bias waveforms consisting of a voltage pulse and a ramp. Narrow energy distributions (< 7 eV FWHM) were demonstrated for ion energies up to 200 eV, as measured using a retarding field energy analyzer (RFEA) in collisionless Ar plasmas.³ By using a low-frequency (100 kHz) waveform, independent control of the ion energy and ion flux was obtained.

Tailored waveform biasing enables precise determination of sputter thresholds which can serve as an input for ALE processes with high synergy and selectivity.¹ Al₂O₃ and HfO₂ sputter thresholds were determined in an Ar plasma as 59 \pm 5 eV and 81 \pm 5 eV, respectively. Surface modification by SF₆ plasma exposure generated a fluorinated surface layer on the Al₂O₃ and HfO₂ films. Fluorination resulted in an increase in sputter yields as well as a reduction of the sputter thresholds to 23 \pm 4 eV and 37 \pm 4 eV, respectively. Evaluating the sputter yield as a function of time shows that an initially higher sputter yield returns toward that of the bulk, indicating full removal of the modified layer. Using this knowledge, an Al₂O₃ ALE process consisting of SF₆ plasma and Ar plasma exposures was evaluated. This work demonstrates that combining self-limiting surface reactions with accurate ion energy control can offer a route to precise and selective ALE.

1. K. J. Kanarik, et al., *J. Phys. Chem. Lett.*, 9, 4814–4821. (2018)
2. S. B. Wang & A. E. Wendt, *J. Appl. Phys.*, 88, 643. (2000)
3. T. Faraz et al., *Journal of Applied Physics*, 128, 213301 (2020)

2:05pm **LI-TuA2-16 Going Beyond Superficial Surface Analysis for Transforming Plants into Value-added Products, Robyn Goacher, Materion Corp.**
INVITED

Preparation of biofuels and value-added bioproducts from lignocellulosic plant matter is an important part of moving away from our global reliance on fossil fuels. Surface analysis of the solid plant starting materials and end products can be complicated by residues from the required chemical or enzymatic treatments and by overlapping signals from plant components themselves. Peak pattern analysis by multivariate statistical approaches such as principle components analysis (PCA) is vital to identifying contaminants from buffers, plasticizers, tape supports, etc, and for distinguishing between fragment ions shared by extractive compounds such as waxes and the main plant biopolymers of cellulose, hemicellulose and lignin. This talk suggests best practices in sample preparation, choice of controls, collection of replicates, and data analysis for lignocellulosic analysis by ToF-SIMS. Accomplishments and gaps in our knowledge of characteristic ions for plant components are described, along with

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examples of how ToF-SIMS has been used to describe the activity of purified enzymes on wood, fungal activity on wood, and chemical treatments of plant matter.

2:25pm **LI-TuA2-20 Molecular Dynamics Study on Damage Formation in Atomic Layer Etching of Si With Halogen Radicals**, *Erin Joy Capdos Tinacba, M. Isobe, S. Hamaguchi*, Osaka University, Japan **INVITED**

Atomic layer etching (ALE) has gained much attention in the past years as an essential technique in fabrication processes of nano-scale semiconductor devices. ALE is a technique to achieve an atomic-scale control of an etching process by separating it into two steps; adsorption and desorption. In the adsorption step, the surface is modified by depositing a mono-layer or thin layer of less reactive molecules. In plasma enhanced ALE (PEALE), the modified layer is removed in the desorption step with the bombardment of energetic ions such as Ar⁺. Ideally these ions should not be energetic enough to continuously etch an unmodified or a clean surface. This is called a self-limiting process of ALE. However, more often than not, non-ideal ALE, i.e., ALE without a complete self-limiting process, is utilized in semiconductor fabrication. In non-ideal ALE, more than one monolayer is removed and the sub-layer of the material may be damaged by excessive ion bombardment. Such damages can be critical on some electronic properties of the materials.

In this work, molecular dynamics (MD) simulation [1] was employed to have a deeper understanding of the reaction mechanisms and damage formation during ALE of Si with F, Cl, or Br adsorption and low-energy Ar⁺ ion bombardment. The Ar⁺ ion energy was varied from 20 to 60 eV. Five cycles of adsorption and desorption steps were simulated and the results were compared with experimental observations [2-4]. It was found that the etch-per-cycle (EPC) value was typically lower during the first cycle compared to the succeeding cycles because the first cycle was mostly spent for the formation of a modified layer. After the first cycle, a reproducible EPC value was observed. The effects of Ar⁺ ion bombardment on the modified surface as well as its Si sub-layer were also investigated. It was observed that, even at low Ar⁺ ion incident energy (20 – 30 eV), the Si sub-layer is damaged in the desorption step and the extent of this damage increases with increasing energy.

[1] E. J. C. Tinacba, *et al.*, Surf. Coat. Technol. 380 (2019), 125032.

[2] H. Sakaue, *et al.*, Mat. Res. Soc. Symp. 222 (1991), 195.

[3] S.-D. Park, *et al.*, Jpn. J. Appl. Phys. 44 (2005), 389.

[4] S. Tan, *et al.*, ECS J. Solid State Sci. Technol., 4(6) (2015), N5010-N5012.

2:45pm **LI-TuA2-24 Variable Polarization, External Magnetic Field, and Spin Resolution for Buried Magnetic Materials Studied by Hard X-Ray Photoemission**, *Shigenori Ueda*, National Institute for Materials Science, Japan **INVITED**

Hard X-ray photoemission spectroscopy (HAXPES) with variable X-ray polarization is useful tool for studying the electronic structures of solids [1,2]. By using horizontal and vertical linear polarized X-ray, the valence band HAXPES spectra show the strong polarization dependence, which allows us to atomic orbital dependent electronic states [1]. For the magnetically ordered materials, HAXPES with left and right handed circularly polarized X-rays permits to probe the magnetic information from the magnetic circular dichroism in core-level photoemission in the element specific way [2]. Since HAXPES is known as a bulk-sensitive probe for electronic structures of solids due to large inelastic mean-free-path of photoelectrons with several keV, it is now possible to probe the electronic states of buried interfaces. In this presentation, the electronic and magnetic states of MgO/Fe interfaces are studied by HAXPES under an applied magnetic field using variable X-ray polarization [3]. The used samples are MgO(2 nm)/Fe(1.5 and 20 nm)/MgO(001), in which the thick and thin Fe films exhibit the in-plane and perpendicular magnetic anisotropies, respectively. For the thin Fe film, the electronic states of the top and bottom interfaces can be probed by HAXPES, while the electronic states of the Fe film inside are dominant in HAXPES. The role of the MgO/Fe interfaces and interface-induced magnetic anisotropy are discussed by comparing the density functional theory calculations. And I will show the results of high-throughput depth-resolved HAXPES combined with total reflection [4] for the MgO(2 nm)/Fe(50 nm)/MgO(001) and spin-resolved HAXPES for buried Fe films [5].

References

[1] S. Ueda and I. Hamada, J. Phys. Soc. Jpn. 86 (2017) 124706.

[2] S. Ueda *et al.*, Appl. Phys. Express 1 (2008) 077003.

[3] S. Ueda *et al.*, Sci. Technol. Adv. Mater. 20 (2019) 796.

[4] S. Ueda, Appl. Phys. Express 11 (2018) 105701.

[5] S. Ueda and Y. Sakuraba, Sci. Technol. Adv. Mater. under review.

3:05pm **LI-TuA2-28 Closing Remarks and Thank You's**, *Mohan Sankaran*, University of Illinois at Urbana-Champaign

Thank you for attending today's session! We also look forward to seeing you tomorrow at 10:00 am EDT for a full day of Live Parallel Sessions. Remember to check out the AVS 67 On Demand Sessions which are available in the mobile app and online scheduler.

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