

# Wednesday Afternoon, November 1, 2017

## Applied Surface Science Division

Room: 13 - Session AS+2D+NS+SA-WeA

### 2D, 3D and nD Imaging of Surfaces, Buried Interfaces and Nanostructures

**Moderators:** Michael Brumbach, Sandia National Laboratories, Kathryn Lloyd, DuPont

2:20pm **AS+2D+NS+SA-WeA1 Laser-SNMS Imaging of Organic and Biological Systems in Two and Three Dimensions., Bonnie June Tyler, A. Pelster, M. Heeger, H.F. Arlinghaus, Universität Münster, Germany**

The introduction of commercial large argon gas cluster ion sputter sources has enabled routine molecular depth profiling and 3D imaging of organic materials with ToF-SIMS. 3D molecular imaging has been demonstrated for a wide variety of organic and biological systems. Despite these advances, sensitivity and quantitation continue to limit applications of the technique for many important systems such as pharmaceuticals. Laser post-ionization of sputtered neutral species is one potential solution to the problems of both low sensitivity and matrix effects.

In this work, we have compared ToF-SIMS and Laser-SNMS for 2D and 3D imaging of several organic systems, including biological samples, pharmaceuticals, and polymeric materials [1-3]. Sample analysis and sputtering were performed using combinations of  $\text{Bi}_3^+$  and  $\text{Ar}_n^+$  ions. Laser post-ionization was performed using either a 157 nm excimer laser or a 195 nm excimer laser. For organic molecules, superior results are obtained using the shorter wavelength laser at lower power density whereas higher power density with the longer wavelength laser is superior for elemental analysis. Increases in ion yield of as much as 4 orders of magnitude have been observed for both elemental and molecular species.

ToF-SIMS and Laser-SNMS show complementary strengths. For high intensity ion signals, ToF-SIMS allows for faster data acquisition. Laser-SNMS, on the other hand, reduces artefacts from topography and matrix effects and enhances measurement efficiency. Higher efficiency reduces the amount of matter that must be sputtered to obtain a given signal, which facilitates measurement of lower concentrations with higher ultimate spatial resolution.

[1] Nees, R. et al., *Biointerphases*, 2016. 11(2): p. 02A305.

[2] Pelster, A., et al., *Analytical Chemistry*, 2016. 88(19): p. 9638-9646.

[3] Pelster, A., et al., *Biointerphases*, 2016. 11(4): p 041001.

2:40pm **AS+2D+NS+SA-WeA2 Distribution of Surfactants and Polymer in a Coating using GCIB-SIMS, Michaeleen Pacholski, Z. Qu, W. Ouyang, The Dow Chemical Company**

Water-based coatings are commonly composed of a latex polymer with additional formulation ingredients such as surfactants, defoamers, etc. The distribution of the additives can have a large role in product performance affecting properties such as adhesion, gloss, water whitening, cohesion, etc. Using GCIB-SIMS profiling the distribution of the additives throughout a film can be shown to relate to the particle size and expected film formation theoretical results. The data from this study show, for the first time, that polymer, surfactant and salts can be monitored as a function of film depth with superior sensitivity and specificity to previous literature studies.

3:00pm **AS+2D+NS+SA-WeA3 Correlation of Morphological and Hyperspectral Characterization Techniques for Nanoelectronic and Energy Applications, Jean-Paul Barnes, A. Priebe, G. Goret, I. Mouton, A. Grenier, G. Audoit, P. Bleuet, Y. Mazel, E. Nolot, Univ. Grenoble Alpes, CEA, LETI, France, S. Legendre, A.L. Tempez, Horiba France S.a.s., France, R. Estivill, M. Juhel, STMicroelectronics, France, S. Duguay, F. Vurpillot, D. Blavette, Normandie Univ, UNIROUEN, INSA Rouen, CNRS, Groupe de Physique des Matériaux, France**

**INVITED**

The integration of a growing variety of materials in increasingly complex structures drives the need to correlate characterization techniques. In this presentation we will discuss the advantages of correlating pairs of techniques such as focused ion beam-time of flight-secondary ion mass spectrometry (FIB-TOF-SIMS) and X-ray computed nanotomography (CNT); atom probe tomography (APT) and electron tomography (ET); and TOF-SIMS depth profiling and plasma profiling time-of-flight mass spectrometry (PPTOFMS).

FIB-TOF-SIMS tomography extends the capacity of TOF-SIMS instruments to analyze large heterogeneous samples of several tens of microns in size as well as porous samples or those with strong surface topography. Standard depth profiling is often not possible as the depth scale information is rapidly

lost in such samples. Examples include copper pillars used in 3-D integration in nanoelectronics and solid oxide fuel cells (SOFCs) which have a complex porous multilayer (sandwich) structure. Whilst FIB-TOF-SIMS provides unique information on the sample chemical composition, there may be morphological artefacts such as curtaining. These may be identified and corrected by analyzing the sample beforehand by X-ray CNT in an SEM. We have developed a method to analyze the same object by both techniques by using novel sample preparation protocols [1].

The correlation of morphological with hyperspectral data can also be applied to APT and ET. APT is increasingly used for the analysis of semiconductor devices because of its unique ability to measure composition in 3D at the atomic scale with high sensitivity. However the APT data sets are often distorted and care must be taken in quantifying composition. The morphological information obtained from analyzing the APT tip beforehand by ET can be used to optimize the parameters when reconstructing the APT data.

PPTOFMS is a rapid depth profiling technique that uses a plasma to etch away the sample and analyze the composition as a function of depth. Unlike SIMS based techniques, the ionization takes place in the plasma and the ratio of ions extracted from the plasma is directly representative (within a factor of 2-3) of the sputtered sample composition. However, the sensitivity and depth resolution are worse than for TOF-SIMS. Combining PPTOFMS with TOF-SIMS depth profiling enables the standard-free quantification and rapid sample screening capabilities of the PPTOFMS to be combined with the sensitivity and high depth and lateral resolution of TOF-SIMS [3].

[1] A. Priebe et al. *Ultramicroscopy*. 173 (2017):10-13.[2] A. Grenier et al *APL* 106, 213102 (2015). [3] A. Tempez et al., *J. Vac. Sci. Technol. B* (2016) 34

4:20pm **AS+2D+NS+SA-WeA7 Insights into Corrosion and Radiation Damage Processes Through 2D and 3D Imaging at the Nanoscale, Karen Kruska, D.K. Schreiber, D.J. Edwards, Z. Zhai, M.J. Olszta, I. Arslan, M.A. Conroy, C. Wang, R.J. Kurtz, S.M. Bruemmer, Pacific Northwest National Laboratory**

**INVITED**

There is an increasing demand for characterization of materials for nuclear reactors with advanced microscopy techniques. Intelligent materials selection requires a fundamental mechanistic understanding of environmental and irradiation damage processes at the nanoscale.

Current and future nuclear power generating systems require materials that can withstand extreme environments. Long-term resistance to environmental degradation is critical for light water reactors as evidenced by stress corrosion cracking concerns in structural alloys for both primary and secondary systems. Resistance to radiation damage further challenges material selection in current and advanced reactors with unique issues for plasma facing components in tokamak-style fusion energy systems where materials must tolerate extended neutron (14 MeV) and  $\text{He}^+$  ion (3.5 MeV) irradiation at extreme temperatures (up to 1300 K). Accumulation of metallic fission products in LWR fuels may cause cracking and has been linked to cladding erosion.

2D analytical electron microscopy techniques have and continue to provide key insights into the evolution of local microstructure and chemistry. More recently, these traditional 2D imaging techniques have been complemented by novel 3D imaging methods, including serial sectioning using a focused ion beam, electron tomography and atom probe tomography. When paired with 2D imaging methods, the 3D microscopy provides deeper insights into the hierarchy of the degradation and damage processes, improved statistical relevance and a greater sensitivity to highly localized effects that were not apparent from 2D imaging alone. Going one step further, dynamic processes (such as oxidation and vacancy injection) can be directly imaged by in situ and operando techniques in transmission electron microscopy. Each technique has its own set of strengths and weaknesses, and in this talk we will emphasize how combining these complementary techniques provides a more comprehensive understanding of material degradation than could be obtained from any individual imaging method.

5:00pm **AS+2D+NS+SA-WeA9 XPS Spectroscopic Imaging of 2D-Materials, Olivier Renault, CEA-Leti, France, H. Kim, EPFL, France, D. Ferrah, UCI, France, N. Fairley, Casa Software, France, M. Gay, CEA-Leti, France, M. Frégnaux, UVSQ, France, A. Kis, EPFL, France**

The recent advent of two dimensional semi-conducting materials of the post-graphene era, such as transition-metal dichalcogenides (TMDs- such as  $\text{MoS}_2$ ,  $\text{WSe}_2$ , ...) has amplified the need for advanced analytical diagnostics. One of the main issues to tackle are directly related to the atomically-thin character of the samples, first concerning the low elemental concentrations and second, the invasive character of most of the characterization techniques implemented. As a photon-probe technique, XPS has a key role to play in the

analysis of TMDs but highly sensitive and versatile microscopic capabilities are needed: this is because the physics of TMDs, notably the indirect-to-direct band gap transition in the monolayer limit, requires spatially-resolved information not only on the chemical composition but also on the electronic band structure. Short analysis times are required because a screening of these properties depending on processing conditions (at the material or the device level) is needed. PEEM-based instruments are the only class of XPS microscopes able to offer both type of analysis. In this presentation, we will review recent studies of 2D materials using XPEEM for chemical imaging and *k*PEEM for band structure imaging, with a particular emphasis on instrumental requirements (excitation source, transmission and detection) and post-processing of the 3D spectroscopic image data sets. The examples will range from graphene doping [1] and cleaning [2], to single layer MoS<sub>2</sub> [3-4], including also novel materials and 2D heterostructures.

This work was performed at the Platform For Nano-Characterization of CEAMINATEC.

- [1] H. Kim, O. Renault *et al.*, *Appl. Phys. Lett.* **105**, 011605 (2014).
- [2] M. Frégnaux, O. Renault *et al.*, *Surf. Interface Anal.* **2016**, 48, 465-469.
- [3] D. Ferrah, O. Renault *et al.*, *Surf. Interface Anal.* **2016**, 48, 451-455.
- [4] H. Kim, M. Frégnaux, A. Kis, O. Renault, *et al.*, *Phys. Rev. B* **34**, 081401 (R) (2016).

5:20pm **AS+2D+NS+SA-WeA10 Carboxylic Acid Headgroups – Towards a New Standard in SAMs**, *Anna Krzykawska*, Jagiellonian University, Poland, *J. Ossowski, T. Żaba, P. Cyganik*, Jagiellonian University, Poland

Self-assembled monolayers (SAMs) prepared from biphenyl-substituted molecules chemisorbed on the Ag(111) substrate via an -SH or -COOH headgroup were characterized using scanning tunneling microscopy (STM), infrared reflection absorption spectroscopy (IRRAS), and X-ray photoelectron spectroscopy (XPS). The objective of this work was to determine which of these headgroups, -SH or -COOH, will provide better 2D ordered SAMs. Importantly, to make such comparison valuable, i.e., to correlate the reduction in the concentration of surface defects with the particular headgroup, we need to compare the two systems, which are chemical analogues, and it would be desired that both systems form SAMs of similar packing density. Only under such conditions can the difference in intermolecular interactions in both systems be minimized to determine the role of headgroup bonding to the substrate in the 2D structural ordering of the resulting SAMs. Our results<sup>1</sup> obtained for monolayers meeting the above criteria show that SAMs with carboxylic headgroups can form, at room temperature and within a very short time of just a few minutes well-ordered 2D structures on Ag(111) with surprisingly large domains. In contrast, the thiol analogue formed at the same temperature reveals poor 2D ordering, with approximately 30 times smaller structural domains. Importantly, this pronounced difference in 2D ordering is observed despite the approximately 300 times longer incubation process of the thiol analogue. We also demonstrate that formation of the thiol analogue at elevated solution temperature (60°C) can significantly increase the size of its domains, which is, however, still approximately 5 times smaller in comparison to the carboxylic analogue formed at room temperature. Moreover, the structure of the carboxylic analogue on Ag(111) also shows better 2D order compared with the former data obtained for the thiol analogue SAMs formed on the Au(111) substrate at room temperature. Only the formation of thiol analogue SAMs at elevated solution temperature (60°C) on the Au(111) substrate with 300 times longer formation time provides comparable 2D ordering to that obtained at the room temperature for the carboxylic analogue SAMs on the Ag(111) substrate.

Our results indicate, therefore, that SAMs based on carboxylic head group can be considered an interesting alternative for the current standard based on the sulfur headgroups, particularly when 2D ordering, SAM fabrication time and stability in the ambient conditions are of great importance.

#### References

- [1] A. Krzykawska, J. Ossowski, T. Żaba and P. Cyganik, *Chem Comm* **2017** accepted

5:40pm **AS+2D+NS+SA-WeA11 2-D and 3-D Characterization of Functionalized Nanostructured Carbons**, *Chilan Ngo, D.R. Diercks, M.B. Strand, M.J. Dzara, J. Hagen, S. Pylypenko*, Colorado School of Mines

Low cost, versatility, and a broad range of properties make carbon a widely studied material with numerous practical applications. Functionalization/doping with heteroatoms is an effective method to tailor the composition and structure of carbon, in order to adjust its properties for various applications. Significant efforts have been dedicated to elucidation of the composition, structure and properties of doped carbon materials, however atomic scale visualization of high-surface area carbons in 3-D has not been achieved. Here, by utilizing a combination of techniques, we focus on understanding the 2-D and 3-D distribution of nitrogen and iron dopants in

high-surface area carbons. Information on surface composition evaluated using X-ray photoelectron spectroscopy (XPS) is complemented by 2-D bulk measurements using energy dispersive X-ray spectroscopy (EDS) through transmission electron microscopy (TEM). 3-D distribution of dopants is studied using atom probe tomography (APT), providing novel insight into the properties of high-surface area carbon materials. This type of investigation necessitated the fabrication of a diverse set of materials with defined shape and morphology, along with variation in the distribution of nitrogen and iron species relative to each other. Nitrogen-doped carbon nanospheres (NCs) were prepared by hydrothermal treatment of resorcinol, formaldehyde, and ethylenediamine, followed by pyrolyzation under flowing nitrogen, producing materials with different dopant concentrations and varied relative distribution of nitrogen functionalities. Iron- and nitrogen-doped nanospheres (FeNCs) were prepared by two routes. For the first set of materials, addition of an iron-containing precursor to the NC synthesis was done prior to hydrothermal treatment, to incorporate Fe throughout the bulk of the nanosphere. The second set is expected to deposit iron only on the surface of the carbon, and is prepared by addition of the iron precursor after the NC pyrolysis, followed by a second pyrolysis. A dual-beam focused-ion beam scanning electron microscope (FIB/SEM) was used to isolate nanospheres into a workable APT tip. Combination of 2-D and 3-D analysis are expected to further the understanding of N-doped carbon materials and N-containing Pt-group metal free catalysts employed in a variety of important catalytic reactions. This work also serves as a foundation to prepare model high-surface area materials that are compatible with *in situ* liquid and electrochemistry TEM techniques, to allow further investigations of these catalytically active materials under conditions relevant to their applications.

6:00pm **AS+2D+NS+SA-WeA12 Characterization of Natural Photonic Crystals in Glitterwing (*Chalcopteryx rutilans*) Dragonfly Wings using 3D TOF-SIMS**, *Ashley Ellsworth, D.M. Carr, G.L. Fisher*, Physical Electronics, *W.W. Valeriano, R.R. de Andrade, J.P. Vasco, E.R. da Silva, A.B.M. Machado, P.S.S. Guimarães, W.N. Rodrigues*, Universidade Federal de Minas Gerais, Brazil

The male Amazonian glitterwing (*Chalcopteryx rutilans*) dragonfly has transparent anterior wings and brightly colored iridescent posterior wings. The colors are important for dragonflies with regard to sexual recognition, mating, and territorial behavior. The source of the varying colors was determined by Valeriano [1] using electron microscopy and optical reflectance to analyze the internal microstructures. SEM and TEM images revealed that the iridescent wings have multiple alternating layers with different electronic densities. The variation of the local color was related to the number and thickness of the layers which varied across the wing. The colors span the visible spectrum with red, blue, and yellow/green regions on the wings. The experimental reflectance was calculated and fitted through the transfer matrix method for the structure obtained from the electron microscopy images. Measurement of the thickness and number of layers is readily achievable by electron microscopy, however it is unable to characterize the chemistry of the different layers giving rise to these natural photonic crystals.

TOF-SIMS is a well-established technique for analyzing the elemental and molecular chemistry of surfaces. TOF-SIMS can now be used to probe the 3D structure and chemistry of a wide variety of organic and inorganic materials, both synthetic and naturally occurring, due to the advent of cluster ion beams such as C<sub>60</sub><sup>+</sup> and large cluster Ar<sub>n</sub><sup>+</sup>. We will present results of 3D TOF-SIMS analyses for both transparent and colored wings to correlate with the electron microscopy and optical results to further the understanding of these natural photonic crystals.

- [1] W.W.Valeriano, Masters dissertation, UFMG, 2016. Retrieved from [http://www.fisica.ufmg.br/posgrad/Dissertacoes\\_Mestrado/decada2010/wesley-valeriano/WesleyWalisonValeriano-diss.pdf](http://www.fisica.ufmg.br/posgrad/Dissertacoes_Mestrado/decada2010/wesley-valeriano/WesleyWalisonValeriano-diss.pdf).

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