

Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+NS+SS+VT-ThA

Progress in Instrumentation and Methods for Spectro-microscopy of Interfaces

Moderators: Jinghua Guo, Lawrence Berkeley National Laboratory, Andrei Kolmakov, National Institute of Standards and Technology (NIST)

2:20pm **CA+NS+SS+VT-ThA1 Helium and Neon Ion Beams for the Imaging and Analysis of Interfaces**, *John A. Notte, C. Guillemier, F. Khanom, B. Lewis*, Carl Zeiss PCS, Inc. **INVITED**

The recently developed ORION NanoFab instrument provides a single platform with He⁺, Ne⁺, and Ga⁺ focused ion beams. The gallium beam is a conventional FIB and offers high currents and high sputter yields for material removal applications such as sample preparation or exposing sub-surface features. The He and Ne ion beams originate from a sub-nanometer ionization volume of the gas field ion source (GFIS) and because of this, can be focused to remarkable small probe sizes, 0.5 nm and 1.9 nm respectively. The He beam is now well established for high resolution imaging with surface sensitivity, long depth of focus, and the ability to image insulating surfaces without a conductive overcoating. The helium beam has also been used successfully in a variety of nanofabrication tasks such as lithographic exposure of resist, fine sputtering, beam chemistry, and precision modification of materials. The neon beam with its intermediate mass provides a higher sputtering yield, and with that, the ability to perform SIMS analysis with an unprecedented small focused probe size. A newly integrated magnetic spectrometer enables analytical capabilities on this same platform, with a lateral resolution limited only by the collision cascade. Features smaller than 15 nm have been detected. Together these complementary imaging modes can be combined to provide insights of morphology and composition at the smallest length scales.

In this talk the underlying technology of the NanoFab-SIMS will be introduced, as will the physics of the beam-sample interactions. The bulk of the presentation will provide a survey of results, both published and new, demonstrating how this instrument can serve in a variety of applications related to interfaces.

3:00pm **CA+NS+SS+VT-ThA3 Interfacial Studies using Ambient Pressure XPS**, *Paul Dietrich, A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany **INVITED**

Over the last decades XPS under Near Ambient Pressure (NAP) conditions has demonstrated its promising potential in a wide variety of applications. Starting from operando studies of surface reactions in catalysis, the applications soon have been enhanced towards studies of processes at liquid surfaces, mainly using freezing/melting cycles, liquid jets or liquid films on rotation disks or wheels. Since more than 15 years, the need for basic studies of fundamental solid-liquid interface chemistry has attracted growing interest. Dip-and-pull experiments at synchrotron sources finally also demonstrated, that in-situ and operando XPS in electrochemical experiments can be realized, significantly contributing to the basic understanding of modern energy converting or storing devices, like batteries, fuel cells, etc.

The development of pure laboratory NAP-XPS systems with optimized sample environments, like special sample holders, Peltier coolers and operando liquid cells combined with full automation and process control provides possibilities for preparation and analysis of a multitude of liquid samples or solid-liquid interfaces on a reliable daily base.

Interfaces of semiconductors with organic solvents are important for production processes and device operation. The first example presented shows the simplicity of obtaining relevant results on Silicon in different organic solvents without the need of highly sophisticated set-ups or special excitation sources beyond Al K_α.

Another example shows an operando study of metal corrosion in acetic acid. Moreover a versatile set-up is presented, allowing for studies of solid-electrolyte interfaces for example in Lithium ion batteries as a simple laboratory experiment.

Finally an outlook is given on the future perspective of applications and scientific contributions of routine operando XPS.

4:00pm **CA+NS+SS+VT-ThA6 Operando Spectroscopy and Microscopy of the Electrode-Electrolyte Interface in Batteries**, *Feng Wang*, Brookhaven National Laboratory **INVITED**

Real-time tracking structural/chemical changes of electrodes in batteries is crucial to understanding how they function and why they fail. However, in real battery systems electrochemical/chemical reaction occurs at varying length scales, leading to changes not only in the bulk but often locally at electrolyte/electrode interface. *In situ* X-ray techniques are typically employed for studying structural changes in the bulk electrodes and often limited by their poor spatial resolution in probing local changes at interface. Herein, we present our recent results from developing new *operando* spectroscopy and microscopy techniques, specialized for studying electrochemical/chemical reaction and structural modification of the solid-electrode surface and interface, *in the presence of the electrolyte and during battery operation*. Examples will be given to show how interfacial reaction during battery operation is visualized directly, allowing gaining insights into electrode/electrolyte design for practical use in batteries. New opportunities for combining *first principles* simulation and deep machine learning to complement and guide experiments will also be discussed.

4:40pm **CA+NS+SS+VT-ThA8 Ultrasensitive Combined Tip- and Antenna-Enhanced Infrared Nanoscopy of Protein Complexes**, *B.T. O'Callahan*, Pacific Northwest National Laboratory; *M. Hentschel*, University of Stuttgart, Germany; *M.B. Raschke*, University of Colorado Boulder; *P.Z. El-Khoury*, Pacific Northwest National Laboratory; **Scott Lea**, Pacific Northwest National Laboratory

Surface enhanced infrared absorption (SEIRA) using resonant plasmonic nanoantennas enables zeptomolar detection sensitivity of (bio)analytes, although with diffraction limited spatial resolution. In contrast, infrared scattering-scanning near-field optical microscopy (IR s-SNOM) allows simultaneous imaging and spectroscopy with nanometer spatial resolution through vibrational coupling to the antenna mode of a probe tip. In this presentation, we discuss our approach combining these two methods to image both continuous and sparse distributions of ferritin protein complexes adsorbed onto IR-resonant Au nanoantennas. The joint tip- and antenna-enhancement yields single protein complex sensitivity due to coupling with the vibrational modes of the bioanalytes. The coupling is revealed through IR s-SNOM spectra in the form of Fano lineshapes, which can be modelled using coupled harmonic oscillators. Through simulations of the recorded hyperspectral images, we extract the optical signatures of protein complex monolayers. This work paves the way for single protein identification and imaging through a combination of tip and antenna-enhanced IR nanoscopy.

5:00pm **CA+NS+SS+VT-ThA9 Imaging and Processing in Liquid Gel Solutions with Focused Electron and X-ray Beams**, *T. Gupta*, National Institute of Standards and Technology (NIST); *P. Zeller, M. Amati, L. Gregoratti*, Elettra - Sincrotrone Trieste, Trieste, Italy; **Andrei Kolmakov**, National Institute of Standards and Technology (NIST)

Gels are porous polymeric scaffolds that can retain high volume fraction of liquids, can be easily functionalized for a specific need, can be made biocompatible and therefore, found numerous applications in drugs delivery, tissue engineering, soft robotics, sensorics, energy storage, etc. We have recently proposed a technique for micro-patterning and high-resolution additive fabrication of 3D gel structures in natural liquid solutions using electron and soft X-ray scanning microscopes [1]. The core of the technology is the employment of ultrathin electron (X-ray) transparent molecularly impermeable membranes that separate high vacuum of the microscopes from a high-pressure fluidic sample. In this communication, we report on effects of the beam and exposure conditions on to the degree of crosslinking of pristine and composite PEGDA hydrogels. We found that cross-linking occurs at very low irradiation doses. The size of the crosslinked area saturates with the dose and bond scission occurs at elevated radiation doses what has been supported with O 1s and C 1s XPS spectra evolution and prior research [2]. These chemically modified regions can be selectively etched what enables an additional partnering option for the gelated features with a spatial resolution of ca 20 nm. Finally, we defined the imaging conditions for guest particles in composite hydrogels in its liquid state during the crosslinking process. We were able to observe the electrophoretic migration of sub 100 nm Au nanoparticles inside the gel matrix.

References

Thursday Afternoon, October 24, 2019

[1] T. Gupta *et al.*, "Focused Electron and X-ray Beam Crosslinking in Liquids for Nanoscale Hydrogels 3D Printing and Encapsulation," *arXiv preprint arXiv:1904.01652*, 2019.

[2] N. Meyerbröker and M. Zharnikov, "Modification and Patterning of Nanometer-Thin Poly (ethylene glycol) Films by Electron Irradiation," *ACS applied materials & interfaces*, vol. 5, no. 11, pp. 5129-5138, 2013.

5:20pm **CA+NS+SS+VT-ThA10 In Situ TEM Visualization of Solution-based Nanofabrication Processes: Chemical Wet-etching and Capillary Forces, Utkur Mirsaidov**, National University of Singapore, Singapore **INVITED**

Controlled fabrication of 3D nanoscale materials from semiconductors is important for many technologies. For example, scaling up the density of the transistors per chip requires the fabrication of smaller and smaller vertical nanowires as channel materials [1]. Two key processes essential to the fabrication of these devices is a precise etching of the nanostructures and the damage-free solution based cleaning (damage occurs during post-clean drying due to capillary forces). However, very little is known about both of these processes because it is extremely challenging to visualize etching and cleaning with solutions directly at the nanoscale. Here, using in situ liquid phase dynamic TEM imaging [2-4], we first describe the detailed mechanisms of etching of vertical Si nanopillars in alkaline solutions [5]. Our design of liquid cells includes a periodic array of patterned nanopillars at a density of $1.2 \times 10^{10} \text{ cm}^{-2}$. We show that the nanoscale chemical wet-etch of Si occurs in three stages: 1) intermediates generated during alkaline wet etching aggregate as nanoclusters on the Si surface, 2) then the intermediates detach from the surface before 3) dissolving in the etchant.

Next, we describe the capillary damage of these high-aspect-ratio Si nanopillars during drying after the solution-phase cleaning. Our results reveal that drying induced damage to nanopillars occurs in three distinct steps. First, as water evaporates from the surface patterned with nanopillars, water film thins down non-uniformly leaving small water nanodroplets trapped between the nanopillars. Second, the capillary forces induced by these droplets bend and bring the nanopillars into contact with each other at which point they bond together. Third, droplets trapped between the nanopillars evaporate leaving the nanopillars bonded to each other. We show that even after the nanodroplets finally evaporate, interfacial water covering the nanopillars act as a glue and holds the pillars together.

Our findings highlight the importance of being able to visualize the processes relevant to nanofabrication in order to resolve the failure modes that will occur more frequently as the device sizes get even smaller in the future.

[1] C. Thelander *et al*, *Mater. Today* 9 (2006), 28–35.

[2] M. J. Williamson *et al*, *Nature Materials* 2 (2003), p. 532.

[3] H. Zheng *et al*, *Science* 324 (2009), p. 1309.

[4] U. Mirsaidov *et al*, *Proc. Natl. Acad. Sci. U.S.A.* 109 (2012), p. 7187.

[5] Z. Aabdin *et al*, *Nano Letters* 17 (2017), p.2953.

[6] This work was supported by Singapore National Research (NRF-CRP16-2015-05).

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