Monday Morning, October 22, 2018

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic
Room 202B - Session MM+AS+NS+PC-MoM

Mechanical, Electrical, Thermal and Optical Systems for In situ TEM (9:00-10:100 am)/Beam Induced Effects and Processing in Liquid/Gas Cells for TEM/SEM (10:40-11:40 am)

Moderators: Suneel Kodambaka, University of California Los Angeles, Olga Ovchinnikova, Oak Ridge National Laboratory

9:00am **MM+AS+NS+PC-MoM-3 Cantilever Substrates for Quantitative Growth Experiments in the Environmental Transmission Electron Microscope***, **Frances Ross**,* IBM T. J. Watson Research Center, MIT **INVITED**

Environmental TEM is an excellent tool for obtaining quantitative information on growth processes and materials transformations. However, it is essential to measure the local temperature, pressure, and other key conditions at the sample location. Well controlled and accurately calibrated *in situ* experiments often make use of specially designed samples and involve various methods for direct measurement of the reaction parameters. Here we describe some of these strategies, but focus on one particular sample design which we suggest is well suited for experiments addressing chemical vapor deposition. In this sample design, growth takes place at the tip of a hairpin cantilever microfabricated from single crystal silicon and heated by direct current. Epitaxial growth is possible on the cantilever surfaces, and deposition on materials such as amorphous silicon nitride is achieved by first coating the cantilever. We discuss how the local temperature and pressure can be measured by monitoring a calibrated growth process. We also discuss how growth can be examined under more complex environments, such as electric fields, using designs involving multiple cantilevers and actuators. We finally discuss approaches to higher pressure than is possible in conventional ETEM by integrating cantilevers in a closed gas cell. Custom substrates based on microfabricated designs appear poised to expand the possibilities of quantitative *in situ* growth experiments to exciting new regimes and materials systems.

9:40am **MM+AS+NS+PC-MoM-5 In Situ Laser Heating and Excitation in the Transmission Electron Microscope: Recrystallization, Grain Growth, Phase Separation and Dewetting in $Ag_{0.5}Ni_{0.5}$ Thin Films***, **Philip D. Rack**,* University of Tennessee Knoxville*; Y Wu,* University of Notre Dame*; C Liu,* University of Tennessee Knoxville*; T Moore, G Magel,* Waviks Inc.*; D Garfinkel,* University of Tennessee Knoxville*; J Camden,* University of Notre Dame*; M Stanford, G Duscher,* University of Tennessee Knoxville

Motivated by the desire to image excited state and high temperature materials phenomena at the nano and atomic scale, Waviks Inc. has recently developed an in situ optical delivery tool for the (scanning) transmission electron microscope (S)TEM. The tool used in these experiments contains two optical delivery channels and is mounted on a Zeiss Libra 200 (S)TEM system. A 785 nm wavelength laser diode system coupled through a 5 µm mode field diameter single-mode fiber is used to deliver >200 mW to the sample surface. The laser can be gated from a few ns to continuous wave (cw) at repetition rates up to 16 MHz. A second optical channel with a 100 µm core diameter broad spectrum multimode fiber is also available for coupling to any excitation source in the wavelength range from 200 to 2100 nm using a standard SMA fiber connector. The system is mounted to a 3 axis (+/- *x,y,z*) nanomanipulator for focusing to the electron/sample coincident point (with sample tilted at ~45 degrees). The system contains a lens system to re-image the fiber optics (1x) at a working distance of ~10 mm, which is long enough eliminate charging and minimizes re-deposition of material. To demonstrate the functionality of the tool, we will show photothermal annealing results of a supersaturated $Ag_{0.5}Ni_{0.5}$ film. We will demonstrate recrystallization, grain growth, phase separation and solid state dewetting of the films via various laser powers, pulse widths, pulse numbers, laser radius. Finally, we will demonstrate interesting in situ excited state phenomena via electron energy gain spectroscopy of plasmonic silver nanoparticles.

10:00am **MM+AS+NS+PC-MoM-6 In situ Transmission Electron Microscopy Study of the Mechanical and Electrical Properties of Single III-V Semiconductor Nanowires***, **Lunjie Zeng**,* Chalmers University of Technology, Gothenburg, Sweden*; C Gammer,* Austrian Academy of Sciences, Austria*; B Ozdol,* Lawrence Berkeley National Laboratory*; T Nordqvist, P Krogstrup,* University of Copenhagen, Denmark*; A Minor,* Lawrence Berkeley National Laboratory*; W Jäger, E Olsson,* Chalmers University of Technology, Gothenburg, Sweden

III-V semiconductor nanowires possess outstanding electronic and mechanical properties that can be utilized in future high-speed electronic devices, solar cells and sensors. To better understand these properties and their relations to the microscopic structure of the nanowires, it is critical to directly correlate the structure and properties of single nanowires. However, the direct characterization of the mechanical and electrical properties of single nanowires, in particular, the correlation between them is still a challenge. In this study, we directly investigate the intrinsic mechanical and electromechanical properties of individual InAs nanowires using in situ transmission electron microscopy (TEM).

Quantitative stress, strain and electrical transport measurements were carried out on single InAs nanowires simultaneously. A Hysitron PI95 nanoindentation TEM holder was used for the in situ TEM study. By using an electrical push-to-pull (EPTP) device in the in situ TEM holder, tensile stress was applied via the nanoindenter in the holder while the force applied on the nanowire was measured by a transducer in the holder. The EPTP device also enables current-voltage (I-V) measurements on single nanowires. Nanoscale lattice strain mapping within the nanowire was performed using scanning transmission electron microscopy (STEM) combined with nanobeam electron diffraction (NBED). NBED diffraction patterns were acquired using a Gatan K2 direct detection camera. Based on the detailed strain and stress measurements, Young's modulus and Poisson's ratio of single InAs nanwires were directly determined. The Young's modulus of single InAs nanowire is smaller than that of the bulk, while the Poisson's ratio of the InAs nanowire is similar as the bulk InAs. The electrical measurements showed that the resistivity of the InAs nanowires decreased continuously with increasing tensile stress. The piezoresistance coefficient of the nanowire was found to be significantly larger than that of bulk InAs. Moreover, significant inhomogeneous strain distribution within the nanowire under stress was unveiled by STEM-NBED strain mapping. The inhomogeneous strain distribution at nanometer scale can increase the resistivity of the nanowire by enhancing electron scattering. The findings demonstrate unique mechanical and electromechanical properties of the nanoscale InAs wires and provide new insights of the correlation between mechanical strain and electrical transport properties in free-standing nanostructures.

Financial support from Swedish Research Council and Nanoscience and Nanotechnology Area of Advance at Chalmers University of Technology are acknowledged.

10:40am **MM+AS+NS+PC-MoM-8 Radiolytic Synthesis of Nanostructured Materials using *In situ* Liquid Cell Microscopy***, **Raymond Unocic**, X Sang, A Belianinov, O Ovchinnikova, K More, S Jesse,* Oak Ridge National Laboratory **INVITED**

There are a wide range of solution-based strategies available for the size- and shape-controlled synthesis of functional nanomaterials for applications in catalysis, energy storage, biomedical, optical, and electronics. To elucidate growth mechanisms, *in situ* liquid scanning transmission electron microscopy (STEM) plays a role for directly imaging and quantifying growth dynamics of nanoparticles from liquid-phase precursors. In this work, we report several strategies for the *active* controlled synthesis of metallic and bimetallic nanoscale architectures using the concept of radiolytic synthesis. In one approach, we developed a direct-write, template-free method to fabricate self-supporting, hollow, metallic nanostructures, and we interpret the formation mechanisms based on direct observations of nucleation and growth. The electron beam used for imaging stimulates radiolysis, promoting the dissociation of water (H_2O) molecules and the formation of complex radical species such as aqueous electrons (e_{aq}^-) and other reducing and oxidizing species. The highly reducing radiolytic species assist in the chemical reduction of metal ions from the precursor solution, resulting in the formation of a metallic nanocrystal seed, which then acts as a catalyst for H_2 gas generation forming a metal encapsulated hollow nanobubble. In another approach, a custom-built electron beam nanopositioning and scan-generator system is used to precisely control the position and electron dose of the focused electron or ion beam to fabricate metallic and bimetallic nanostructured materials. These strategies enable fundamental electron beam interaction studies and open a new pathway for direct-write nanolithography from liquid-phase solutions.

This research was supported by the Center for Nanophase Materials Sciences, which is a United States Department of Energy Office of Science User Facility.

11:20am **MM+AS+NS+PC-MoM-10 Electron Beam Induced Cross-Linking in Liquid Hydrogels***, **Tanya Gupta**, A Kolmakov,* National Institute of Standards and Technology (NIST)

Advances in additive manufacturing of bio-friendly polymeric materials over the last decade has revolutionized the diverse fields like rapid prototyping, tissue engineering, drug delivery etc. The technology currently relies on laser, thermal or UV induced 3D printing. Other triggers with similar effects can in principle be used as ionizing radiation to carry out the crosslinking. In this work we explore the use of electron beam to perform 3-D patterning at mesoscale and explore its potential towards rapid prototyping. In particular, knowledge of electron interaction with the printing ink allows us to predict effect of various control parameters like beam energy , current and dwell time on the topology of the features formed. A Monte-Carlo simulation coupled with a rigorous kinetic model is built to study the interplay of dose distribution, total interaction volume and diffusional effects of the active radiolytic species.

11:40am **MM+AS+NS+PC-MoM-11 Nanoscale Chemical Reactor Based on Localized Surface Plasmon Energy in Environmental Transmission Electron Microscope***, **Canhui Wang**[1], W Yang,* UMD/NIST*; R Sharma,* National Institute of Standards and Technology

Miniaturizing chemical processes in a research context has many advantages, including the ability to examine the reaction at atomic resolution, the reduced usage of costly and/or hazardous chemical reagents, and the ability to be integrated into analytical devices. [1-2] However, the current efforts of miniaturizing chemical processes have been limited by achievable minimum reaction volume and the lack of precision control over the reaction locations. Herein, we demonstrate a nanoscale chemical reactor utilizing localized surface plasmon (LSP) resonance as the energy source in an environmental transmission electron microscope (ETEM). This approach allows us to confine the reaction within proximity of the nanoparticle while taking advantage of the high spatial resolution capability of the electron microscope to monitor the reaction.

Plasmonic nanoparticles, such as Au or Al, are placed in a reactive environment inside the ETEM. The composition and partial pressure of the gases are controlled by a gas handling system. Electron energy-loss spectra (EELS) imaging is used to acquire both elemental and LSP maps from the same nanoparticle. This allows the mapping and quantification of different gas adsorption on the nanoparticle surface. The energy required for the reaction of interest is provided by the LSP resonance excited by the high energy electron beam. The reaction location is confined within proximity of the nanoparticle due to the local field enhancement of the LSP resonance. Using a non-negative matrix factorization machine learning algorithm [3], we map the energy transfer pathways from the electron beam to the nanoparticle at nanometer spatial resolution and 0.08 eV energy resolution. The temperature distribution of the nanoparticle is monitored with few-nanometer spatial resolution using time-resolved EELS. Reaction processes, including morphological changes and transition of crystalline phases, are monitored using aberration-corrected atomic-resolution movies. By utilizing LSP resonance to initiate the reaction, we show that chemical processes can be confined in a nanometer scale volume, and modulated by electron flux. Important factors of the reaction, including composition of the reactants, adsorption of gases, transfer of energy, change of temperature, as well as reaction dynamics, can be monitored with nanometer or atomic resolution. Our approach paves the way to understanding a wide range of chemical reactions at the atomic scale.

References:

[1] Abdelgawad, Mohamed, et al. Lab on a Chip 9.8 (2009): 1046-1051.

[2] Williamson, M. J., et al. Nature materials 2.8 (2003): 532.

[3] O. Nicoletti, et al. Nature 502.7469 (2013): 80.

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[1] **NSTD Postdoc Finalist**

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic
Room 202B - Session MM+AS+NS+PC+SS-MoA
X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA-1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies***, **Luca Gregoratti**, M Amati, P Zeller,* Elettra-Sincrotrone Trieste, Italy **INVITED**

Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectromicroscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 µm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA-3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy***, **Jared Bruce**, J Hemminger,* University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent, $Fe^{2+}_{(aq)}$, change with depth relative to the air/liquid interface. The chemical state is also sensitive to "spectator" ions in the solution. The presence of Cl^- leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA-4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy***, S Nemsak,* Forschungszentrum Juelich GmbH, Germany*; E Strelcov,* NIST Center for Nanoscale Science and Technology*; **Tomas Duchon**,* Forschungszentrum Juelich GmbH, Germany*; H Guo,* National Institute of Standards and Technology*; J Hackl,* Forschungszentrum Juelich GmbH, Germany*; A Yualev,* NIST Center for Nanoscale Science and Technology*; I Vlassiouk,* Oak Ridge National Laboratory*; D Mueller, C Schneider,* Forschungszentrum Juelich GmbH, Germany*; A Kolmakov,* NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable Cu+ ions.

3:40pm **MM+AS+NS+PC+SS-MoA-8 Practical Liquid Cell Microscopy - Opportunities and Challenges***, **Daan Hein Alsem**, K Karki,* Hummingbird Scientific*; T Mefford, W Chueh,* Stanford University*; N Salmon,* Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent SiNx membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 01.M $CuSO_4$ and 20 mM $K_3Fe(CN)_6$/20 mM $K_4Fe(CN)_6$ in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA-10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy***, **Hongxuan Guo**, A Yulaev, E Strelcov,* National Institute of Standards and Technology (NIST)/ University of Maryland, College Park*; A Tselev,* CICECO and Department of Physics, University of Aveiro,Portugal*; A Kolmakov,* National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods [1], and more recently with X-ray spectroscopy [2, 3], as well as scanning probe microscopy[4].

In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.[5,6]. We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

Reference

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[2]. M. Favaro, B. Jeong, P. N. Ross, J. Yano, Z. Hussain, Z. Liu and E. J. Crumlin, Nature Communications 7(2016), 12695

[3]. M. A. Brown, Z. Abbas, A. Kleibert, R. G. Green, A. Goel, S. May, and T. M. Squires, Physical Review X 6(2016), 011007

[4]. J. M. Black, M. Zhu, P. Zhang, R. R. Unocic, D. Guo, M. B. Okatan, S. Dai, P. T. Cummings, S. V. Kalinin, G. Feng, and N. Balke, Scientific Reports 6 (2016), 32389

[5]. A. Yulaev, H. Guo, E. Strelcov, L. Chen, I. Vlassiouk, A Kolmakov, ACS applied materials & interfaces 9 (2017), 26492-26502

[6]. H. Guo, E. Strelcov, A. Yulaev, J. Wang, N. Appathurai, S. Urquhart, J. Vinson, S. Sahu, M. Zwolak, and A. Kolmakov, Nano Letters,17(2017), 1034–1041

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic
Room Hall B - Session MM-TuP

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic Poster Session

MM-TuP-1 In-situ Low Energy Electron Microscopy at Near Ambient Pressures*, **Thomas Schulmeyer**,* SPECS Surface Nano Analysis GmbH

Low-energy electron microscopy (LEEM) is a spectromicroscopy technique which allows the study of dynamic processes at surfaces and interfaces, such as thin-film growth, surface reactions, and phase transitions. With the FE-LEEM P90 from SPECS, which is based on the instrument design by Rudolf Tromp from IBM, lateral and energy resolution of below 5 nm and 250 meV, respectively, can be achieved. Depending on the excitation source and the settings on the instrument, a variety of different imaging modes are possible: mirror electron microscopy, low energy electron diffraction (LEED), phase contrast imaging, reflectivity contrast, dark field imaging and bright field imaging, as well as photoelectron emission microscopy and spectroscopy. As a new development, the technical capabilities of LEEM and PEEM have been extended toward near ambient conditions by developing a special objective lens concept and sample chamber geometry. This enables the analysis of materials and devices under near ambient conditions and even in situ during operation. For this a Laser heater allows for sample temperatures up to 800°C during the measurements. The technical realization will be presented in detail. Furthermore experimental results will be shown on Graphene, Silicon under Nitrogen atmosphere. First results from real surface reactions will be discussed.

MM-TuP-2 NanoESCA III: Recent Progress and Applications*, M Merkel, N Weber, M Escher, T Kühn,* FOCUS GmbH, Germany*; **Marten Patt**,* Scienta Omicron GmbH, Germany

During the last years essential progress has been made in developing the technique of energy filtered photoemission electron microscopy (PEEM). Different approaches of imaging energy filtering have been introduced and developed more and more.

One of the most essential achievements was in 2003 the invention [1] and design of the imaging double energy analyser (IDEA), an aberration compensated band pass filter. This PEEM dedicated energy filter became the core element of the NanoESCA III instrument. Its unique design allows for high quality imaging of band pass filtered PEEM images at UV light excited threshold energies for e.g. work function mapping up to hard x-ray energies (HAXPEEM) [2] for bulk sensitive measurements.

Both the real and the momentum space of a sample can be imaged by direct switching in between both modes. The latter so called momentum microscopy, acquiring the full band structure from a microscopic sample region of interest, becomes a more and more popular alternative to the common ARPES set-up using a single hemispherical analyser. Besides elimination the major component of the analyser's spherical aberration, the tandem arrangement also largely retains the time structure of the electron signal, unlike a single hemispherical analyser which can be helpful with time resolving experiments.

We will show some recent applications [3] and instrumental set-ups taking advantage of these possibilities.

[1] D. Funnemann, M. Escher, European Patent EP 1 559 126 B1, US patent US 7 250

599 B2

[2] Patt et al., Rev. Sci. Instrum. 85, 113704 (2014)

[3] see e.g.: Ming-Wie Chen et al., npj 2D Materials and Applications (2018) 2:2 ; doi:10.1038/s41699-017-0047-x

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