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.

[1] **NSTD Postdoc Finalist**

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