

Thursday Morning, November 2, 2017

Nanometer-scale Science and Technology Division

Room: 19 - Session NS+AS+EM+MI+SP+SS-ThM

Nanoscale Imaging and Characterization

Moderators: Stephane Evoy, University of Alberta, Canada, Indira Seshadri, IBM Research Division, Albany, NY

8:00am **NS+AS+EM+MI+SP+SS-ThM1 Characterizing Optoelectronically-Active Molecules via STM Imaging and Advanced Raman Spectroscopy Techniques**, *J. Schultz, P. Whiteman, Z. Porach, Nan Jiang*, University of Illinois at Chicago

In response to the ever increasing demand for cleaner, cheaper energy generation, significant efforts have been made to fabricate and characterize materials that can be used for optoelectronic devices. Porphyrins, phthalocyanines, and their derivatives have been involved in many surface studies to investigate their optoelectronic properties for use in organic photovoltaics and other optoelectronic devices, such as organic light-emitting diodes (OLED). Our research take place in a commercial ultrahigh vacuum (UHV) scanning tunneling microscopy (STM) chamber. Molecules were evaporated onto various single crystal substrates at a base pressure of 10^{-10} torr. Different surface-supported structures were imaged via STM at sub-molecular resolution, allowing the competition of molecule-substrate and molecule-molecule interactions to be investigated.

In addition to imaging via STM, we also performed spectroscopy experiments in the forms of UHV Tip Enhanced Raman Spectroscopy (TERS), supplementing vital vibrational information at single-molecule spatial resolution. These tools provide a complete picture of the system in question, allowing our lab to answer previously unknown questions regarding the molecule-molecule interactions in order to characterize the molecule's exciton-generating and electron-transferring properties at a fundamental level.

8:20am **NS+AS+EM+MI+SP+SS-ThM2 BCC to FCC Phase Transition of Pd_xCu_{1-x} at Nanoscale**, *Xiaoxiao Yu*, Carnegie Mellon University, A. Gellman, Carnegie Mellon University, W.E. Scott Institute for Energy Innovation

One of the most interesting characteristics of alloy nanoparticles (NPs) is that they can have different phases from those of the bulk. In the bulk phase diagram of Pd_xCu_{1-x}, there exists a composition range, $0.35 < x < 0.55$, over which a B2 phase (ordered body centered cubic, CsCl structure) is formed at $T < 873$ K, in spite of the fact that pure Pd and Cu both have face centered cubic (FCC) bulk crystal structures. An experimental methodology has been developed for determining the phase behavior of Pd_xCu_{1-x} size and composition spread nanoparticle (SCSNP) libraries. Spatially resolved X-ray photoemission spectroscopy (XPS) was used to map the Cu $2p_{3/2}$ core level shifts (CLS) with respect to the value for pure Cu across composition space on the bulk Pd_xCu_{1-x} alloy. The result has shown that the Cu $2p_{3/2}$ binding energy decreases monotonically with increasing Pd at.% in the FCC phase. There is additional discontinuous CLS over the composition range from 0.35 to 0.55 Pd at.%, where the B2 phase forms. Therefore, the Cu $2p_{3/2}$ core level binding energy measured by XPS can be used to distinguish between the ordered B2 phase and disordered FCC phase. The Pd_xCu_{1-x} SCSNP library on a Mo substrate was prepared using a rotatable shadow mask deposition tool previously developed by our group. After annealing the Pd_xCu_{1-x} alloy thin film to 700 K, the additional CLS over the composition range, $0.35 < x < 0.55$, has been observed at a film thickness > 6 nm, which suggests the formation of B2 phase. However, at a film thickness between 4 – 6 nm, the Cu $2p_{3/2}$ binding energy decreases monotonically across composition space which suggests that only FCC phase exists for alloy films in this thickness range. Because the FCC phase is more densely packed than the B2 phase, the surface tension in this thickness regime can drive a conversion from the ordered B2 phase back to the randomly distributed FCC solid solution. More interestingly, the additional CLS over the composition range from 0.35 to 0.55 Pd at.% reoccurs at a film thickness < 4 nm, which suggests the formation of B2 phase. This observation is the result of dewetting of the Pd_xCu_{1-x} NPs after heating at 700 K for 30 mins, and the size of dewetting NPs exceeds 6 nm where the close-packed FCC phase is stabilized. Dewetting of Pd_xCu_{1-x} NPs is validated by the appearance of the substrate Mo XPS signal at a film thickness < 4 nm. This comprehensive experimental study of the phase behavior for Pd_xCu_{1-x} alloy NPs will be correlated with their catalytic activity across composition and size spaces to accelerate the development of alloy NPs for catalytic applications.

8:40am **NS+AS+EM+MI+SP+SS-ThM3 Hybrid Environmental Transmission Electron Microscope: An Integrated Platform for In situ Imaging and Spectroscopies**, *Renu Sharma*, NIST **INVITED**

Environmental transmission electron microscopes (ETEM) and TEM holders with windowed reaction cells, enable in situ measurements of the dynamic changes occurring during gas-solid and/or liquid-solid interactions. The combination of atomic-resolution images and high spatial and energy resolution has successfully revealed the nucleation and growth mechanisms for nanoparticles, nanowires, carbon nanotubes and the functioning of catalyst nanoparticles. While TEM-based techniques are ideally suited to distinguish between active and inactive catalyst particles and identify active surfaces for gas adsorption, we still must answer the following questions: (1) Are our observations, made from an area a few hundred nanometers in extent, sufficiently representative to determine the mechanism for a specific reaction? (2) Is the reaction initiated by the incident electron beam? (3) Can we determine the sample temperature accurately enough to extract quantitative kinetic information? And (4), can we find efficient ways to make atomic-scale measurements from the thousands of images collected using a high-speed camera. The lack of global information available from TEM measurements is generally compensated by using other, ensemble measurement techniques such as x-ray or neutron diffraction, x-ray photoelectron spectroscopy, infrared spectroscopy, Raman spectroscopy etc. However, it is almost impossible to create identical experimental conditions in two separate instruments to make measurements that can be directly compared.

We have designed and built a unique platform that allows us to concurrently measure atomic-scale and micro-scale changes occurring in samples subjected to identical reactive environmental conditions by incorporating a Raman Spectrometer into the ESTEM. We have used this correlative microscopy platform i) to measure the temperature from a $60 \mu\text{m}^2$ area using Raman shifts, ii) to investigate light/matter interactions in plasmonic particles iii) to act as a heating source, iii) to perform concurrent optical and electron spectroscopies such as cathodoluminescence, electron energy-loss spectroscopy and Raman. We have developed an automatic image-processing scheme to measure atomic positions, within 0.015 nm uncertainty, from high-resolution images, to follow dynamic structural changes using a combination of algorithms publicly available and developed at NIST. This method has been proven to capture the crystal structure fluctuations in a catalyst nanoparticle during growth of single-walled carbon nanotube (SWCNT). Details of the design, function, and capabilities of the optical spectrum collection platform and image processing scheme will be presented.

9:20am **NS+AS+EM+MI+SP+SS-ThM5 Critical Dimension Metrology by Localization Optical Microscopy**, *C.R. Copeland, C.D. McGray, J.C. Geist, J.A. Liddle, B.R. Ilic, Samuel Stavis*, NIST

Optical microscopy methods of localizing subresolution emitters are broadly useful in many fields from biology to nanofabrication. Precision and accuracy are fundamental for localization measurements. Subnanometer precision is readily achievable for many emitters and can elucidate structure and motion at atomic scales, but is potentially false precision in the absence of calibrations that enable corresponding accuracy, particularly over a wide field for imaging and tracking. Whereas improving localization precision generally requires counting more photons by increasing emitter intensity and stability, improving localization accuracy presents diverse challenges in the calibration of an optical microscope as a measurement system. This involves not only its discrete components but also their interaction during a measurement. Such calibration is complex, motivating the development of practical devices and methods to facilitate the process, which we present here.

First, we characterize a complementary metal oxide semiconductor (CMOS) camera, enabling full use of its dynamic range and megapixel array. Next, we fabricate aperture arrays by electron-beam lithography and test them as calibration devices, exploiting their uniformity and stability. Then, we refine localization analysis, presenting a novel estimator and accommodating saturation. Finally, we evaluate aberrations of our optical system, including field curvature, distortion, and others that break the symmetry of the point spread function. After calibrating our system in this way, we validate our widefield measurements and demonstrate critical dimension localization microscopy (CDLM) of aperture arrays, and answer open questions about the apparent motion of nanoparticle fiducials. Our study casts new light on localization microscopy at subnanometer scales.

Our study also highlights the importance of nanoscale fabrication and metrology in achieving localization accuracy. Previous studies have applied aperture arrays for lens evaluation but have not quantified their critical dimensions, in particular the array pitch. This is essential to ensure that electron-optical aberrations do not propagate as errors through the calibration and correction of photon-optical aberrations. Moreover, the application of

CDLM to aperture arrays provides useful information on the effects of dose delivery and beam scanning to optimize the future nanofabrication of reference materials.

9:40am **NS+AS+EM+MI+SP+SS-ThM6 Tunable Emission from Nanophotonic Structures in a Modified SEM: Characterizing Smith Purcell Radiation Generation from the VUV to the Near IR, Steven Kooi, I. Kaminer, A. Massuda, M. Soljačić, C. Roques-Carmes, MIT**

We present theoretical predictions and experimental results of multiple order Smith-Purcell radiation in a variety of samples from periodic high aspect ratio silicon nanowire structures to engineered metasurfaces using low-energy electrons (2.5 -20 keV) in a modified scanning electron microscope. The samples emit photons in a controlled way and we demonstrate optical emission from the VUV to the near IR, opening a pathway to building a fully tunable optical source that we intend to extend into the soft X-Ray regime.

11:00am **NS+AS+EM+MI+SP+SS-ThM10 Ultrafast Optical Response of Graphene/LaAlO₃/SrTiO₃ Heterostructure, L. Chen, E. Sutton, J. Li, M. Huang, J.F. Hsu, B. D'Urso, University of Pittsburgh, J.W. Lee, H. Lee, C.B. Eom, University of Wisconsin-Madison, P. Irvin, Jeremy Levy, University of Pittsburgh** **INVITED**

The unique electronic and optical properties of graphene make it a promising device in terahertz (THz) regime. Another 2D electron system, the complex-oxide heterostructure LaAlO₃/SrTiO₃, has been shown to exhibit great promise for control and detection of broadband THz emission at extreme nanoscale dimensions¹. Recently, we have successfully integrated these two platforms: we have created graphene/LaAlO₃/SrTiO₃ structures with (1) high mobility in the graphene channel² and (2) oxide nanostructures patterned directly underneath the graphene layer³. Here we describe new experiments that probe graphene with this nanoscale THz spectrometer using ultrafast optical techniques. This unprecedented control of THz radiation at 10 nm length scales creates a pathway toward hybrid THz functionality in graphene/LaAlO₃/SrTiO₃ heterostructures.

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11:40am **NS+AS+EM+MI+SP+SS-ThM12 Single-Molecules Fluorescence Spectroscopy and Lifetime with Simultaneous Super-resolution Imaging for Materials Science Applications, James Marr, CNST/NIST and University of Maryland, M. Davanço, CNST/NIST, S.J. Stranick, NIST, B.R. Ilic, J.A. Liddle, CNST/NIST**

We have developed a widefield imaging system that measures single-molecule position, orientation, lifetime and fluorescence spectra. We achieve this by combining conventional super-resolution imaging using an sCMOS detector with a unique, photon-counting, wide-field, high-temporal, high-spatial resolution, high-throughput, three-dimensional detector (H33D). The use of dual-objectives maximizes the fluorescent photon flux to each camera. Individual fluorophore point-spread functions collected by the sCMOS detector provide position and orientation information, while the 100 ps timing resolution of the H33D detector enables us to make precise lifetime measurements of the same fluorophore. By incorporating a diffraction grating into the beam path of the sCMOS camera we can simultaneously record both a zero-order image of each fluorophore for position and orientation measurement, and a wavelength-dispersed image that provides single-molecule spectroscopic data. The sensitivity of fluorophore lifetime, spectroscopic behavior, orientation, and position to dynamic processes in soft materials with nanosecond, millisecond, and second timescales, respectively, enables us to collect three-dimensional, local structure-property information that would otherwise be impossible to obtain. We have fabricated unique structures that enable us to accurately determine the influence of metallic and high-refractive index materials on fluorophore lifetime and point-spread function shape. Our far-field system, combined with these nanoengineered structures, permit minimally-perturbative measurements to be made on individual fluorophores. We apply our imaging system to probe the nanoscale behavior of polymers in nanocomposite materials and to investigate

fluorophore response to structured samples consisting of thin, high-refractive index materials.

12:00pm **NS+AS+EM+MI+SP+SS-ThM13 Atomic Scale Surface Effects of Controlled Crystal Structure in III-V Semiconductor Nanowires: Preferential Surface Alloying and Local Electronic Properties., J. Knutsson, M. Hjort, Lund University, Sweden, P. Kratzer, University Duisburg-Essen, Germany, J. Webb, S. Lehmann, K.D. Thelander, Lund University, Sweden, C.J. Palmstrom, UCSB, R. Timm, Anders Mikkelsen, Lund University, Sweden**

Despite the many III-V nanowire (NW) technologies under current development, be it solar cells and light emitting diodes or high speed/low power electronics, there are still only few studies of their surfaces. The atomic scale structure and morphology of NW surfaces are however central in determining their functionality, due to the inherently large surface to bulk ratio. In addition, III-V NWs can be tailored with segments of both the cubic zinc blende (ZB) and hexagonal wurtzite (WZ) structures and in a variety of materials combinations. This allow experimental access to nanocrystallite surfaces and interfaces not found in the bulk. We have demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices [1-5]. We now use these methods for studying atomic scale surface structural changes and impact on local electronic properties on both GaAs and InAs NWs at room temperature and at 5K.

We explore the surface diffusion and alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases. We find that Sb preferentially incorporates into the surface layer of the -terminated Wz segments rather than the -terminated Wz segments. Density functional theory calculations verify the higher surface incorporation rate into the Zb phase and find that it is related to differences in the energy barrier of the Sb-for-As exchange reaction on the two surfaces. These findings demonstrate a simple processing-free route to compositional engineering at the monolayer level along NWs.

Using low temperature STM/S we measure local density of states of atomic scale tailored Zb segments in Wz InAs nanowires down to the smallest possible crystal lattice change. We find that Zb crystal phase signatures can be seen in the density of states both on the conduction and valence band sides as well as in the band positions down to the smallest possible Zb segment. Additionally we find indications of confined state effects due to the difference in bandgap between Wz and Zb. Finally we explore the stability of InAs NWs with atomic scale STM during the application of voltages through the NWs in a device configuration. We observe that applying realistic voltages to InAs NWs results in removal of atomic scale defects and smoothening of the morphology.

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- [6] O. Persson et al., *Nano Letters* **15** (2015) 3684

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