Tuesday Afternoon, October 31, 2017

Scanning Probe Microscopy Focus Topic
Room: 10 - Session SP+AS+MI+NS+SS-TuA

Probe-Sample Interactions
Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **SP+AS+MI+NS+SS-TuA1 Atomic Manipulation of Atomic Oxygen on Graphene**, *H.K. Kim, T. Ahn, T.S. Youn, D.G. Lee, **Tae-Hwan Kim***, Pohang University of Science and Technology, Republic of Korea
Graphene, a single sheet of sp^2-bonded carbon atoms, is considered as a promising material for future electronic devices especially due to its superior electron mobility as well as mechanical stability. For various applications of graphene, however, the electronic structure has to be tuned and the diverse functionalization is strongly required. In particular, it has been well known that the oxidation of graphene can alter its electronic and optical properties remarkably. We have investigated the atomic oxygen chemisorbed on the epitaxial graphene using scanning tunneling microscopy (STM). The high-resolution topographic images and tunneling spectroscopy spectra reveal distinctive electronic states of oxygen atoms, which bridge two adjacent carbon atoms and make graphene epoxide. More importantly, using the STM tip can controllably induce the local removal and the rearrangement of the atomic oxygen by applying the appropriate biases. The technique is similar to the STM nanolithography, which has been reported, for example, for hydrogenated Si(001). In principle, a combination of the controlled desorption and hopping of atomic oxygen can be employed to design the local electronic property on graphene with atomic-scale precision, which may lead to advanced atomic-scale devices based on graphene.

2:40pm **SP+AS+MI+NS+SS-TuA2 Revealing Distance-Dependence of Chemical Interactions and Image Contrast Reversal in Noncontact Atomic Force Microscopy: A Case Study on Highly Oriented Pyrolytic Graphite**, *O.E. Dagdeviren*, J. Goetzen, E.I. Altman, **UdoD. Schwarz***, Yale University
The structural and chemical nature of surfaces governs a material's ability to interact with its surrounding. Designing nanodevices requires tailoring surfaces to meet specific needs and revealing underlying fundamental principles, which determine surface reactivity at the atomic scale. A particularly interesting case occurs when the surface site exhibits varying attraction with distance. To shed light on this issue, noncontact atomic force microscopy experiments combined with scanning tunneling microscopy experiments have been carried out where the evolution of the atom-specific chemical interaction leads to contrast reversal in the force channel. Due to the importance of sp^2-hybridized carbon surfaces in functional nanostructures, we have used highly ordered pyrolytic graphite surface and metal probe tips as the model system. Our experiments reveal that at larger tip-sample distances, carbon atoms exhibit stronger attractions at hollow sites while upon further approach, hollow sites become energetically more favorable [1,2]. The analysis suggests the fundamental factors promoting contrast reversal are local varying decay lengths and an onset of repulsive forces that occurs for distinct surface sites at different tip-sample separations. In addition to these, a change of the hybridization state of carbon atoms from sp^2 to sp^3 under the influence of an approaching reactive probe can also result in contrast reversal. Our experiments address the unexpected nature of contrast reversal due to different governing mechanisms, which are determined by local properties of the sample as well as interacting materials. Combined with in-depth computational analysis, such experiments will lead to a deeper understanding of the fundamental effects that govern how materials interact with their surroundings at sub-nanometer scale. Entangling these fundamental principles with design will enable fabrication and synthesis of better nanodevices with graphene and other layered materials as well as nanotubes.

[+] Author for correspondence: omur.dagdeviren@yale.edu

[1] O.E. Dagdeviren et al, Nanotechnology 27, 065703 (2016)

[2] O.E. Dagdeviren et al, Nanotechnology, 27, 485708 (2016)

3:00pm **SP+AS+MI+NS+SS-TuA3 Absence of a Band Gap at Metal-Monolayer MoS$_2$ Interface**, *Abhay Pasupathy*, Columbia University **INVITED**
Abstract: High quality electrical contact to semiconducting transition metal dichalcogenides (TMDCs) such as MoS_2 is key to unlocking their unique electronic and optoelectronic properties for fundamental research and device

applications. Despite extensive experimental and theoretical efforts reliable ohmic contact to doped TMDCs remains elusive and would benefit from a better understanding of the underlying physics of the metal-TMDC interface. Here we present measurements of the atomic-scale energy band diagram of junctions between various metals and heavily doped monolayer MoS_2 using ultra-high vacuum scanning tunneling microscopy (UHV-STM). Our measurements reveal that the electronic properties of these junctions are dominated by 2D metal induced gap states (MIGS). These MIGS are characterized by a spatially growing measured gap in the local density of states (L-DOS) of the MoS_2 within 2 nm of the metal-semiconductor interface. Their decay lengths extend from a minimum of ~0.55 nm near mid gap to as long as 2 nm near the band edges and are nearly identical for Au, Pd and graphite contacts, indicating that it is a universal property of the monolayer semiconductor. Our findings indicate that even in heavily doped semiconductors, the presence of MIGS sets the ultimate limit for electrical contact

4:20pm **SP+AS+MI+NS+SS-TuA7 Imaging of MOS Interface Trap Distribution using Local Deep Level Transient Spectroscopy Based on Scanning Nonlinear Dielectric Microscopy**, *N. Chinone, **Yasuo Cho***, Tohoku University, Japan
Physical properties of metal-oxide-semiconductor (MOS) interface are critical for semiconductor devices. There are several techniques for characterizing MOS interface properties. Deep level transient spectroscopy (DLTS)is one of powerful techniques capable of macroscopic quantitative evaluation of trap density at/near MOS interface (D_{it}). But it is easily imagined that actual trap is not homogeneously distributed, but has two dimensional distributions in atomic scale and even in mesoscopic scale. Therefore, it is very important to characterize MOS interface microscopically. Unfortunately, it is impossible to observe such inhomogeneity by using conventional macroscopic DLTS method.

In this paper, a new technique for local DLTS imaging based on scanning nonlinear dielectric microscopy (SNDM) is proposed. This method enables us to observe two dimensional distribution of trap density at/near MOS interface and is demonstrated with oxidized SiC wafer.

45-nm-thick thermal oxide layers were formed on three Si-faces of 4°-off n-type 4H-SiC wafers. One of them was labeled as #S-45-1. The other two wafers were subjected to post-oxidation annealing (POA) in nitric oxide (NO) at different conditions as follows: 1250°C for 10 minutes (#S-45-2), 1150°C for 60 minutes (#S-45-3). The average D_{it} values of these samples were measured by conventional High-Low method, which showed that the D_{it} of #S-45-1 was highest and that of #S-45-3 was lowest.

These three samples were scanned on 1.5x1.5μm^2 square area with a resolution of 30x30 pixels and analyzed using the proposed local DLTS method.

By analyzing the acquired images, time-constant τ and magnitude of transient capacitance response were obtained at each pixel. Highest brightness was obtained from #S-45-1 and lowest one was obtained from #S-45-3, which is consistent with macroscopically obtained result. Furthermore, in the local DLTS images, we detected dark and bright areas, which can be translated as two dimensional trap distribution.

Next, quantitative imaging of D_{it} was performed. Distributions of D_{it} for τ = 0.3 μs and 3 μs were imaged for all samples. The time constants 0.3 μs and 3 μs correspond to energy depth of 0.24 eV and 0.30 eV below the conduction band, respectively. All images have dark and bright areas with feature size of a few 100 nm. In addition, the images with different time constant showed different distribution, which implies that the distribution of interface traps depends on time constant, or suggests the physical origin of interface trap with different energy level is different.

This local DLTS technique can contribute to understanding microscopic physical properties of MOS interface.

4:40pm **SP+AS+MI+NS+SS-TuA8 Quantum State Readout of Individual Quantum Dots by Electrostatic Force Detection**, *Yoichi Miyahara, A. Roy-Gobeil, P.H. Grutter*, McGill University, Canada
Electric charge detection by atomic force microscopy (AFM) with single-electron resolution (e-EFM) is a promising way to investigate the electronic level structure of individual quantum dots (QD). The mechanical oscillation of the AFM tip modulates the energy of the QDs, causing single electrons to tunnel back and forth between QDs and an electrode. The resulting oscillating electrostatic force changes the resonant frequency and damping of the AFM cantilever, enabling electrometry with a single-electron sensitivity. While quantitative electronic level spectroscopy is possible by sweeping the bias

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* NSTD Student Award Finalist

voltage, charge stability diagram of the QD can be obtained by scanning the AFM tip around the QD. e-EFM technique can be applied for the investigation of individual colloidal nanoparticles and self-assembled QDs without defining nanoscale electrodes. e-EFM is a quantum electromechanical system where the back-action of a tunneling electron is detected by AFM and can also be regarded as a mechanical analog of admittance spectroscopy with a radio frequency resonator, which is emerging as a promising tool for quantum state readout for quantum information processing. In combination with the topography imaging capability of the AFM, e-EFM is a powerful tool for investigating nanoscale material systems which can be used as quantum bits such as nanowires and single molecules and dopants.

1 Y. Miyahara, A. Roy-Gobeil and P. Grutter, Nanotechnology 28, 064001 (2017).

5:00pm SP+AS+MI+NS+SS-TuA9 Cryogenic Near-field Imaging and Spectroscopy at the 10-Nanometer-scale, *Max Eisele*, A. Huber, neaspec GmbH

Near-field microscopy and spectroscopy has become one of the key technologies for modern optics, combining the resolving power of AFM based measurements with the analytical aspects of optical microscopy and spectroscopy. Near-field microscopy has already proven itself vital for modern nanomaterials and has been used in applications such as chemical identification [1], free-carrier profiling [2], or the direct mapping of propagating plasmons [3,4], phonon [5], and exciton polaritons [6]. Key information like the local conductivity, intrinsic electron-doping, absorption, or the complex-valued refractive index can routinely be extracted from these measurements with a spatial resolution of down to 10 nanometer.

In combination with femtosecond light sources, near-field microscopy has also enabled ultrafast pump-probe experiments [7] with a combined 10-femtosecond temporal and 10-nanometer spatial resolution [8]. Carrier-relaxation dynamics in black phosphorus [9] or graphene [10] are just two examples of the broad range of potential applications for ultrafast near-field nano-spectroscopy.

Within this talk we will introduce the newest technological breakthrough in the field of near-field optics - Cryogenic near-field imaging and spectroscopy. This novel approach has been pioneered by the group of Dimitri Basov at Columbia University and UC San Diego using a home-build cryogenic near-field microscope with a temperature range of 24 – 300 Kelvin. For the first time, this microscope has been capable to spatially resolve the insulator-to-metal phase transition of V2O3 with <25nm spatial resolution [11]. Extending ambient near-field measurements to cryogenic temperatures will open a complete new world for nanoscale optical microscopy and spectroscopy, enabling the direct mapping of phase-transitions in strongly correlated materials or the detection of low-energy elementary excitations at the surface of solid-state systems. A first commercial cryogenic system with a temperature range down to 10 Kelvin is now available from neaspec [12] making this technology broadly available to the community.

References:

[1] I. Amenabar et al., Nature Comm. 8, 14402 (2017)

[2] J. M. Stiegler et al., Nano Lett. 10, 1387 (2010)

[3] J. Chen et al., Nature 487, 77 (2012)

[4] Z. Fei et al., Nature 487, 82 (2012)

[5] E. Yoxall et al., Nature Photon. 9, 674 (2015)

[6] F. Hu et al., Nature Photon. 11, 356 (2017)

[7] M. Wagner et al., Nano Lett. 14, 894 (2014)

[8] M. Eisele et al., Nature Photon. 8, 841 (2014)

[9] M. Huber et al., Nature Nanotech. 12, 207 (2017)

[10] G. X. Ni et al., Nature Photon. 10, 244 (2016)

[11] A. S. McLeod et al., Nature Phys. 13, 80 (2017)

[12] www.neaspec.com

5:20pm SP+AS+MI+NS+SS-TuA10 Atomic Scale Proximity Effect at a Molecular Superconductor-Metal Boundary, *KyawZin Latt*, S. Khan, Ohio University, *A. Ngo*, Argonne National Laboratory, *H. Chang*, Ohio University, *A. Hassanien*, J. Stefan Inst., Slovenia, *L. Curtiss*, Argonne National Laboratory, *S.W. Hla*, Ohio University and Argonne National Laboratory

How a superconductor interacts with metal at a superconductor-metal boundary is vital for fundamental understanding of important phenomena such as Andreev reflection, and proximity effect. Here we investigate how the cooper pairs from a charged transfer based molecular superconducting cluster interact with 2-D surface state electrons from Ag(111) surface at the atomic scale using tunneling microscopy, tunneling spectroscopy, and atomic/molecular manipulation schemes at low temperatures in an ultrahigh

vacuum environment. The superconducting molecular clusters here are composed of a few molecular chains formed by BETS (donors) and GaCl4 (acceptor). In STM images, these molecular clusters appear as ordered parallel chains resembling the 'rafts'. Using scanning tunneling microscope (STM) manipulation, small molecular clusters are repositioned on the surface at desired locations. From the tip height signals, the dynamics of molecular clusters during their movements across the surface has been unveiled. Repeated manipulation experiments reveal that the rafts move only along [211] surface directions with single atomic site hops. Tunneling spectroscopy measurements across metal superconductor boundary provides variation of electron structures highlighting how surface state electrons interact with the superconducting clusters.

5:40pm SP+AS+MI+NS+SS-TuA11 Breaking the Time Barrier in Scanning Probe Force Microscopy: Fast Free Force Reconstruction (F³R) for Non-contact SPM, *L. Collins, Stephen Jesse*, S.V. Kalinin, Oak Ridge National Laboratory

In the past 3 decades since its invention, the atomic force microscope (AFM) has offered unparalleled insight into both nanoscale structure and surface functionality. At the same time, the spatial resolution afforded by AFM tip is counterpoised by the slow detection speeds compared to other common microscopy techniques (e.g. optical, scanning electron microscopy etc.). This ultimately limits AFM and related measurements to static or quasi-static processes.

In this presentation, we outline a novel time resolved AFM imaging approach, referred to as Fast free force recovery (F³R)[1] utilizing big data capture and analytics. F³R-AFM is based on the G-mode acquisition platform [2] and allows direct reconstruction of the tip-sample forces with much higher time resolution (~μs) than possible using standard AFM detection methods (~ms). We describe how fast data acquisition, coupled with multivariate statistical denoising methods can be harnessed to overcome the widely viewed temporal bottleneck in AFM, the mechanical bandwidth of the cantilever. Finally, we will demonstrate quantitative recovery of tip-sample forces with <10 μs time resolution, free from influences of the cantilever ring-down as well as discussing the fundamentally time and information limits of the approach.

[1] Collins, Liam, Mahshid Ahmadi, Ting Wu, Bin Hu, Sergei V. Kalinin, and Stephen Jesse. "Breaking the Time Barrier in Kelvin Probe Force Microscopy: Fast Free Force Reconstruction Using the G-Mode Platform." *ACS nano* (2017).

[2] Belianinov, Alexei, Sergei V. Kalinin, and Stephen Jesse. "Complete information acquisition in dynamic force microscopy." *Nature communications* 6 (2015).

6:00pm SP+AS+MI+NS+SS-TuA12 Ultrafast G Mode-Kelvin Probe Force Microscopy and its application to probing ionic transport mechanisms in perovskite solar cells., *Liam Collins, S. Jesse, S.V. Kalinin*, Oak Ridge National Laboratory

Kelvin probe force microscopy (KPFM) is crucial technique for the joint investigations of structural, electronic, and electrochemical functionality on materials ranging from ferroelectrics, and photovoltaics, to battery and fuel cell devices. While KPFM has shown extraordinary success for quantification of equilibrium *or quasistatic* functionalities, this level of information is not sufficient for describing electroactive materials or devices involving fast (< ms) relaxation processes. Practically, the detection methodologies adopted in classical KPFM limit the temporal resolution of the measurement (e.g. ~1-10 MHz photodetector stream is down sampled to a single readout of surface potential per pixel).

In this presentation General Acquisition mode (G-Mode) KPFM[1-3] will be introduced. It will be shown that by harnessing big data acquisition and analytics, it is possible to extract dynamic information on the local electrochemical processes with nanometer spatial and microsecond time resolution. Furthermore, the G-Mode KPFM approach is immediately implementable on all AFM platform, allows capture of numerous channels of information simultaneously (*e.g.* capacitive and potential channels), as well as providing increased flexibility in terms of data exploration across frequency, time, space, and noise domains.

Finally we harness these imaging capabilities to explore non-linear ionic transport in organic-inorganic halide perovskites. We will present imaging of spatio-temporal charge dynamics at the perovskite/electrode interface with <20 μs time resolution and ~10s nm spatial resolution. As will be outlined, based on our observations, we determine that the transport behavior of these materials is considerably more complex than previously argued.

[1] Collins, Liam, et al. "Multifrequency spectrum analysis using fully digital G Mode-Kelvin probe force microscopy." *Nanotechnology* 27.10 (2016): 105706.

[2] Collins, Liam, et al. "Full data acquisition in Kelvin Probe Force Microscopy: Mapping dynamic electric phenomena in real space." *Scientific reports* 6 (2016): 30557.

[3] Collins, Liam, et al. "Breaking the Time Barrier in Kelvin Probe Force Microscopy: Fast Free Force Reconstruction Using the G-Mode Platform." *ACS nano* (2017).

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