

## Scanning Probe Microscopy Focus Topic

### Room 10 - Session SP+AS+NS+SS-MoM

#### New Imaging and Spectroscopy Methodologies

**Moderators:** Wonhee Ko, Oak Ridge National Laboratory, An-Ping Li, Oak Ridge National Laboratory

8:20am **SP+AS+NS+SS-MoM-1 Charge Transport through Nanostructures measured with a Multi-Tip STM, Bert Voigtländer**, Forschungszentrum Juelich, Germany **INVITED**

The use of Multi-Tip STM for transport measurements is another step in the recent paradigm shift in scanning probe microscopy transforming from "just imaging" to detailed measurements at the nanoscale. Multi-Tip STM is an ideal technique to study electronic properties, while a current is running through a nanostructure/nanodevice.

We demonstrate how three requirements have to be combined to perform nanoscale charge transport measurements, using the Multi-Tip STM technique: (a) a stable, versatile, and easy to operate Multi-Tip STM instrument, as well as (b) electronics and software, which allow any possible "concerted" Multi-Tip measurements, and last but not least (c) the new method Multi-Tip STM also requires new methodologies for data analysis.

We demonstrate the capabilities of the Multi-Tip STM method to reveal fundamental nanoscale charge transport properties by the following examples: (a) Mapping of resistance profiles and corresponding doping profiles along freestanding GaAs nanowires, (b) measurement of the surface conductivity at semiconductor surfaces, (c) identification of resistivity dipoles in nanoscale potential maps around defects, using scanning tunneling potentiometry, (d) disentangling *in situ* top and bottom conductance of a topological insulator thin film by gate dependent measurements.

9:00am **SP+AS+NS+SS-MoM-3 Robust High-Resolution Imaging and Quantitative Force Spectroscopy in Vacuum with Tuned-Oscillator Atomic Force Microscopy, Omur Dagdeviren, J Goetzen**, Yale University; *H Holscher*, Karlsruhe Institute of Technology (KIT), Germany; *E Altman, U Schwarz*, Yale University

Since the first demonstration of atomic resolution in ultrahigh vacuum more than twenty years ago, frequency modulation-based noncontact atomic force microscopy (FM-NC-AFM) has significantly matured and is now routinely applied to study problems that benefit from high-resolution surface imaging. In FM-NC-AFM, control of the tip's vertical position is accomplished by detecting a shift in the cantilever's resonance frequency upon approach to the sample. Consistently ensuring reliable distance control during extended data acquisition periods has nevertheless remained challenging, as most FM-mode-based control schemes employ three feedback loops that may interfere. As a consequence, sample throughput in FM-NC-AFM is often low compared to ambient condition AFM, where the easy-to-implement amplitude-modulation (AM) control scheme is predominantly used. Transfer of the AM methodology to high-resolution measurements in vacuum is, however, difficult as with AM-AFM, instabilities during approach are common. In addition, the lack of viscous air damping and the related significant increase of the cantilever's quality factor generate prolonged settling times, which cause the system's bandwidth to become impractical for many applications. Here we introduce a greatly simplified approach to NC-AFM imaging and quantitative tip-sample interaction force measurement that prevents instabilities while simultaneously enabling data acquisition with customary scan speeds by externally tuning the oscillator's response characteristics [1]. After discussing background and basic measurement principle, examples for its application to a variety of sample systems are provided [1,2,3,4]. A major advantage of this operational scheme is that it delivers robust position control in both the attractive and repulsive regimes with only one feedback loop, thereby carrying the potential to boost the method's usability.

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

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

[3] O.E. Dagdeviren et al, *Physical Review B*, 93, 195303 (2016)

[4] O.E. Dagdeviren et al, *Advanced Materials and Interfaces*, 4, 1601011 (2017)

9:20am **SP+AS+NS+SS-MoM-4 Electrical Transport Measurements with Atomically Precise Probes, Markus Maier, J Koebler, R Thiel, M Fenner, A Pirou, D Stahl, T Roth**, Scientia Omicron GmbH

A major challenge in the development of novel devices in nano- and molecular electronics is their interconnection with larger scaled electrical circuits. Local electrical probing by multiple probes with precision on the atomic scale can significantly improve efficiency in analyzing electrical properties of individual structures on the nano-scale without the need of a full electrical integration.

The LT NANOPROBE is a sophisticated instrument that merges the requirements of a 4-probe system, efficiently and precisely navigated by a scanning electron microscope (SEM) and at the same time satisfies the needs for high performance SPM. The excellent stability in the pm range allows for atomic resolution in STM and nc-AFM (QPlus) and expands applications from electrical probing on the nanometer scale towards tunneling and force spectroscopy and the creation of atomically precise structures. The system is operated near thermal equilibrium and temperatures below 5K, specifically also during simultaneous SEM imaging and navigation. The system has been developed towards an extremely low thermal drift in the range of 100pm/h, which is the most important ingredient to allow for enough measurement time on extremely small structures.

We will present measurements that prove the performance level of the instrument, specifically the low thermal drift and stability as well as QPlus AFM measurements, which become important if nanostructures are deposited on an insulating substrate for a better electrical decoupling. We will also show the newest technology improvements, such as high frequency capabilities and optical access for pumped probe experiment. Future technology challenges as well as applications and scientific drivers for this type of scientific instrumentation will be discussed.

9:40am **SP+AS+NS+SS-MoM-5 Planar Two-probe Scanning Tunneling Spectroscopy Measurements at the Atomic Level, Marek Kolmer**, Jagiellonian University, Krakow, Poland **INVITED**

We present our recent results obtained on the new Scientia-Omicron low temperature ultra-high vacuum 4-probe STM (LT-Nanoprobe). This unique machine is equipped with 4 STM scanners able to operate on the same surface simultaneously with the stability of the *state-of-art* single tip low temperature STMs [1].

Firstly we show our methodology for fine relative positioning of two STM probes on a surface with unprecedented atomic precision and with a lateral exact probe to probe distance below 50 nm. Secondly we discuss our design of the 2-probe STM experiment, in which both tips are kept in tunnelling conditions above a grounded sample. Then, by applying a DC bias voltage between probes in the described configuration we can detect a probe to probe DC current signal. Moreover, we add a small AC component to a varied DC bias voltage and by demodulation of resulting current signals on each of the probes, we extract corresponding  $dI_1/dV_1$  (vertical) and  $dI_2/dV_1$  (planar) STS signals. Our method allows a direct testing of the electronic transport properties of atomic-scale structures in a *fully planar* geometry, what is shown on an example of a model system: bare Ge dimer wires on Ge(001) surface. In this case we determine ballistic charge transport regimes in the atomic wires by systematic 2-probe spectroscopic experiments on the probe to probe distances below 50 nm.

Finally, we discuss perspectives for application of the above methodology in characterization of molecular structures, i.e. molecular wires obtained by the on-surface synthesis approach on metal oxide surfaces [2-4].

Support by the European Commission under PAMS project (contract no. 610446) and by the Polish Ministry of Science and Higher Education (contract no. 0341/IP3/2016/74) are gratefully acknowledged.

[1] J. Yang et al., *Eur. Phys. J. Appl. Phys.*, **73**, 10702 (2016)

[2] M. Kolmer et. al., *Angew. Chem. Int. Ed.*, **52**, 10300 – 10303 (2013)

[3] M. Kolmer et. al., *Chem. Comm.*, **51**, 11276 – 11279 (2015)

[4] G. Vasseur et al., *J. Am. Chem. Soc.*, **138**, 5685–5692 (2016)

10:40am **SP+AS+NS+SS-MoM-8 An Ultrafast Scanning Probe Microscopy Technique for Imaging Polarization Switching in Ferroelectric Materials, Suhaz Somnath, S Kalinin, S Jesse**, Oak Ridge National Laboratory

Polarization switching in ferroelectric and multiferroic materials underpins the next generation of electronic devices such as tunneling devices, field effect transistors, and race-track memories. The switching mechanisms in these materials are extremely sensitive to local defects and structural imperfections at the micro- and nanometer scale, which have undesirable

# Monday Morning, October 30, 2017

effects on ferroelectric domains. These considerations led to the development of Piezoresponse Force Microscopy (PFM) for imaging and manipulating local polarization states. In PFM, a micro-cantilever with a conductive tip is brought into contact with the sample surface. Periodic bias applied to the tip deforms the sample, which in turn causes the cantilever to vibrate, and these vibrations are recorded using an optical setup in the microscope. The current state-of-art PFM imaging and spectroscopy techniques measure the bias dependent material deformation either at a single frequency (using a lock-in-amplifier) or over a narrow band of frequencies thereby discarding valuable information from higher vibrational modes of the cantilever and multiple harmonics. As an extension, PFM spectroscopy techniques suffer from serious compromises in the measurement rate, voltage and spatial resolutions since they require the combination of a slow ( $\sim 1$  sec) switching signal and a fast ( $\sim 1 - 10$  msec) measurement signal. The slow measurement speed results in undesirable compromises between the imaged area, spatial resolution, and voltage resolution.

We report on a new voltage spectroscopy technique applied to PFM that rapidly acquires dense 2D maps of local hysteretic material response. This technique combines the acquisition of the complete information about the cantilever response with intelligent signal filtering techniques to enable direct measurement of material strain in response to the probing bias. Our technique enables precise spectroscopic imaging of the polarization switching phenomena 3,500 times faster than currently reported methods. By rapid acquisition of a large number of hysteretic loops on very dense grids, this technique will enable significant insight into nanoscale polarization dynamics and phenomena such as polarization fatigue or local wall displacements that remain difficult to study at the desired spatial and temporal scales, and are crucial for integration of ferroelectric nanostructures in future electronic devices.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

11:00am **SP+AS+NS+SS-MoM-9 Direct Probing of the Graphene-Electrolyte Double Layer Potential**, *Evgheni Strelcov*, NIST Center for Nanoscale Science and Technology / University of Maryland; *A Tselev*, University of Aveiro, Portugal; *H Guo*, *A Yulaev*, NIST Center for Nanoscale Science and Technology / University of Maryland; *I Vlasiouk*, Oak Ridge National Laboratory; *N Zhitenev*, *W McGehee*, *B Hoskins*, *J McClelland*, *A Kolmakov*, NIST Center for Nanoscale Science and Technology

Solid-liquid interfaces play an instrumental role in a broad range of natural phenomena in biological, hydrological, chemical and electrochemical systems. The latter include energy conversion and storage applications, such as fuel cells, supercapacitors, electrochromic devices, and batteries, whose performance strongly depends on the state of the solid-liquid interface. Key elements of this interfacial behavior are the formation of the electrical double layer (EDL), ionic transport through it, ionic adsorption, and Faradaic processes. Thus, understanding the structure and properties of the EDL is of critical importance. Despite more than a century of research on the EDL, its molecular structure and electrode potential dependence remain the subject of frontier research. Only a handful of experimental techniques, including surface force and spectral methods, are currently available for direct probing of the EDL, but even they do not offer adequate spatial resolution.

Here, we report on direct measurement of the EDL potential in a copper (II) sulfate electrolyte with Kelvin Probe Force microscopy (KPFM). The aqueous electrolyte is placed in a multichannel array, consisting of high aspect ratio, 2  $\mu\text{m}$  diameter channels, sealed at the bottom and capped with bilayer graphene at the top. The system can be imaged *in vacuo* with high resolution scanning electron microscopy and KPFM, correlatively. The graphene membrane acts as both an electrode and a seal that prevents the electrolyte from evaporating into the vacuum. The KPFM probe scans over the subnanometer graphene membrane of individual channels and records potential of the EDL formed at the electrified graphene-electrolyte interface. Both graphene and bottom platinum electrode can be biased to modulate the response of the system to polarization. The collected data are compared to numerical simulation of EDL formation.

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acknowledge support of the National Research Council Research Associateship Program.

11:20am **SP+AS+NS+SS-MoM-10 Quasiparticle Interference Mapping of ZrSiS**, *Michael Lodge*, University of Central Florida; *G Chang*, *B Singh*, National University of Singapore; *J Hellerstedt*, *M Edmonds*, Monash University, Australia; *D Kaczorowski*, Polish Academy of Sciences; *M Hosen*, *M Neupane*, University of Central Florida; *H Lin*, National University of Singapore, Singapore; *M Fuhrer*, Monash University, Australia; *B Weber*, Nanyang Technological University, Singapore; *M Ishigami*, University of Central Florida

3D Dirac semimetals are a class of materials whose bulk electronic states are protected by topology, presenting intriguing new systems in which to study the rich physics of the quasiparticles that they host. One such system is the nodal line Dirac semimetal, wherein the conductance and valence bands have a line-like crossing along a closed loop in momentum space and disperse linearly in the vicinity of the resulting line node. This configuration gives rise to the prediction of exotic phenomena such as spin vortex rings, diverging mobility in the limit of vanishing chemical potential, and a linearly increasing dependence of the conductivity on temperature. Many of these compounds have their line node located hundreds of meV above the Fermi level, making direct observation of the line-node inaccessible to experimental techniques such as angle resolved photoemission spectroscopy (ARPES). We employ spectroscopic imaging scanning tunneling microscopy (SI-STM) at 4.5K to visualize the quasiparticle interference with point defects in zirconium silicon sulfide (ZrSiS). In combination with numerical modeling, we identify six groups of quasiparticle scattering vectors allowed within the material, and show that topological protection of the electronic bands is relaxed in the presence of certain defects. We also estimate the location of the line node.

## Scanning Probe Microscopy Focus Topic Room 10 - Session SP+2D+AS+NS+SS-MoA

### Probing Electronic and Transport Properties

**Moderators:** Phillip First, Georgia Institute of Technology, Chuanxu Ma, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA-1 Probing Atomic and Electronic Structures of 2D Electronic Materials and their Heterostructures, *Chih-Kang Shih***, University of Texas at Dallas **INVITED**

The emerging atomic layer materials offer a remarkably wide range of building blocks of nanostructures ranging from metals (e.g. graphene), large gap insulators (BN), to semiconductors (transition metal dichalcogenides and black phosphorous). Key advantages of these van der Waals materials include a broad span of energy gaps, flexibility of stacking different types of materials to form heterostructures, tunability in material properties by doping and strain, and the relative ease of integration with other electronic and photonic devices. This talk will be focused on the usage of scanning tunneling microscopy and spectroscopy to probe the atomic and electronic structure of transition metal dichalcogenides (TMDs) and their heterostructures, including both vertical and lateral structures.

I will first introduce a comprehensive form of scanning tunneling spectroscopy (STS) which allows us to probe not only the quasi-particle band gaps but also the critical point energy locations and their origins in the Brillouin Zone (BZ) can be revealed using this comprehensive form of STS. By using this new method, we reveal the systematic trend of the critical point energies for TMDs due to atomic orbital couplings, spin-orbital coupling and the interlayer coupling. By using the vertically stacked MoS<sub>2</sub>/WSe<sub>2</sub>, I will show how interlayer coupling can be used as a new designing parameter to create a lateral 2D electronic superlattices. I will then turn attention to MoS<sub>2</sub>/WSe<sub>2</sub> lateral heterostructure where I will show a novel method to probe 2D strain tensor and how the strain changes the band profile as well as the band alignment at the interface.

2:20pm **SP+2D+AS+NS+SS-MoA-3 SP-STM Study of Antiferromagnetic CuMnAs Thin Film, *Giang Nguyen***, Oak Ridge National Laboratory; *P Wadley*, *R Campion*, *K Edmonds*, University of Nottingham, UK; *F Maccherozzi*, *S Dhesi*, 3Diamond Light Source, UK; *T Jungwirth*, University of Nottingham, UK; *A Li*, Oak Ridge National Laboratory

Antiferromagnetic (AFM) tetragonal CuMnAs thin films have attracted great research interest recently, largely due to the capability of manipulating and detecting of their AFM states with ordinary electric current. Here we report a study on a CuMnAs thin film, grown epitaxially on GaP(001) substrates, using Spin-Polarized Scanning Tunneling Microscopy (SP-STM). An arsenic capping layer is used to protect the sample during transferring through the air which is able to be subsequently removed from the surface by thermal annealing. Atomic resolution STM topographic images of CuMnAs surface are achieved which shows an interesting surface reconstruction. Scanning tunneling spectroscopy (STS) is performed to explore the electronic structure of the thin film as well at the surface step edge. SP-STM study in combination with X-ray magnetic linear dichroism-photoelectron emission microscopic (XMLD-PEEM) measurements provides further understanding of the antiferromagnetic domain structure.

This research was conducted at the Center for Nanophase Materials Sciences, which is sponsored at Oak Ridge National Laboratory by the Scientific User Facilities Division, Office of Basic Energy Sciences, U.S. Department of Energy.

2:40pm **SP+2D+AS+NS+SS-MoA-4 Probing Spin-Dependent Chemical Potential in Topological Insulator by Spin-Polarized Four-Probe Scanning Tunneling Microscopy, *Wonhee Ko***, *S Hus*, Oak Ridge National Laboratory; *Y Chen*, Purdue University; *A Li*, Oak Ridge National Laboratory

Conversion between the charge and the spin signal is a core technology for detection of many spin-related phenomena and for the realization of spintronic devices. Topological insulators are promising candidate for such purpose because of their surface states with non-trivial spin texture. The surface states electrons have the spin and the momentum locked to each other, so the electrical current can induce the uneven shift in the spin-dependent chemical potential for different spin directions. In this talk, we utilized spin-polarized four-probe scanning tunneling microscopy to probe the spin-dependent chemical potential of the topological insulators. Utilizing ferromagnetic tips and variable probe-spacing measurements, we

detected non-vanishing spin-dependent chemical potential induced by the charge current. Various tip and surface conditions were tested to confirm its origin from the spin of charge carriers through the surface states. The result demonstrates the generation of excessive spins only by electrical means in topological insulators, which would become the critical component for the future spintronic applications.

This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

3:00pm **SP+2D+AS+NS+SS-MoA-5 Spin-charge Transport Phenomena on the Atomic Scale Studied by Multi-probe STM, *Christoph Tegenkamp***, Leibniz Universität Hannover, Germany **INVITED**

Low dimensional metallic structures, e.g. quantum wires and films on surfaces, reveal fascinating phenomena of condensed matter physics. Among others, 2D-superconductivity, formation of charge density waves and topologically protected edge states were realized lately with atomic precision and directly probed by electronic transport. Generally, the surface science approach benefits from the fact that the low dimensional systems can be comprehensively characterized and manipulated in view of their atomic structure and electronic bands. This is a prerequisite to understand electronic transport on the atomic scale.

In this talk I will introduce the technique of surface sensitive transport by means of 4-tip STM technique and highlight some recent examples of our group from seemingly different fields, e.g. spintronic, correlated materials and mesoscopic physics. The talk covers spin-orbit coupling related phase transitions in quasi 1D atomic wire structures (Au/Si(553), Pb/Si(557) [1,2]) as well as ballistic transmittance of electrons in epitaxially grown graphene nanostructures on SiC(0001) [3-5].

[1] C. Tegenkamp, et.al. PRL 109, 266401 (2012)

[2] C. Brand, et.al. , Nat. Comm. 6, 8118 (2015)

[3] J. Baringhaus ,et.al., Nature 506, 349 (2014)

[4] J. Baringhaus et.al. Sci. Rep. (Nature) 5, 9955 (2015)

[5] J. Baringhaus et.al. PRL. 116, 3186602 (2016)

4:00pm **SP+2D+AS+NS+SS-MoA-8 Site-specific Superconducting Atomic Contacts Studied by Scanning Tunneling Microscopy, *Yukio Hasegawa***, The Institute for Solid State Physics, The University of Tokyo, Japan **INVITED**

In the trend of miniaturization of devices, electrical conductance through atomic-scale contacts is of significant importance for practical application of atom switch and single molecular devices. Because of unknown atomic geometry at the junction, however, the measured conductance often fluctuates. Here in this study we have studied the conductance properties of atomic superconducting point contact with precise control of contact geometry to investigate atomic details of conductance channel formation through it.

Using a low-temperature scanning tunneling microscopy (STM), we measured the conductance between the tip and sample surface from the tunneling to contact regimes [1]. By precisely positioning the tip on atomically specific sites of a sample surface such as on-top and hollow sites, site-specific conductance evolutions were obtained. We found using a Pb tip and Pb thin film as contact forming materials the conductance at point contact is larger at hollow site than at on-top site. Furthermore, it is found that the relation of the conductance measured is reversed just before the contact formation; at 20 pm away from the contact the conductance of the hollow site is smaller than the on-top site. These peculiar conductance behaviors can be explained by the attractive chemical force and subsequent conductance channel formation between the tip apex atom and surface atoms of the thin film.

Since the measurements were performed at low temperature (1.6 K) below the superconducting critical temperature of both materials, we obtained the evolution of the Josephson current and subharmonic in-gap structures due to multiple Andreev reflection (MAR) in the conductance spectra. From the analysis of the MAR structures, the complete set of transmission probability of conduction channels, which is often called personal identification number (PIN) of the junction as it determines all the coherent transport properties, was successfully extracted [2]. We found again site dependent evolution of transmission probabilities and the number of active conduction channels at the contact formation. We will discuss on the mechanism of channel formations based on comparison with the results of theoretical analysis.

References

[1] H. Kim and Y. Hasegawa, Phys Rev Lett 114, 206801 (2015)

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[2] H. Kim, M. Kawamura, T. Kato, T. Ozaki, and Y. Hasegawa, in preparation.

4:40pm **SP+2D+AS+NS+SS-MoA-10 The Difference between Electron and Hole Dopant of Magnetic Element to the Superconductivity in BaFe<sub>2</sub>As<sub>2</sub>**, *Qiang Zou, L Li, A Sefat, D Parker, Z Gai*, Oak Ridge National Laboratory

The effect of magnetism and spin excitation in the Fe-based superconductors (FeSC) is crucial to understand their superconductivity. Both electron-(Ni) and hole-(Cr) dopant of magnetic elements could lead to suppression of the magnetic/structural phase transition in BaFe<sub>2</sub>As<sub>2</sub>. However, the Cr doped BaFe<sub>2</sub>As<sub>2</sub> doesn't show the superconductivity. Using scanning tunneling microscopy/spectroscopy, here, we compared the electronic properties of BaFe<sub>2-x</sub>NixAs<sub>2</sub> and BaFe<sub>2-x</sub>Cr<sub>x</sub>As<sub>2</sub> at various temperatures. Our results will shed the light on the microscopic understanding of relation between the superconductivity and magnetism in the FeSC. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:00pm **SP+2D+AS+NS+SS-MoA-11 Rapid Measurement of I-V Curves in Scanning Probe Microscopy via Bayesian Inference**, *S Somnath, K Law, R Archibald, S Kalinin, S Jesse, Rama Vasudevan*, Oak Ridge National Laboratory

Current-voltage (IV) curve acquisition is the oldest and most common spectroscopic method implemented on virtually every scanning probe microscope (SPM) available. Though in use for three decades, the basic measurement has not altered substantially in this time-frame, with the current being detected during DC pulses applied to the SPM tip. Such measurements include both a delay time after each DC voltage change (to reduce parasitic capacitance influence), as well as an integration time, to reduce noise, limiting typical measurements to a few Hz at most. Here, we introduce a new method for IV curve acquisition, based on an AC-excitation of the SPM tip, in combination with full information acquisition from the current amplifier and Bayesian inference. IV curves are acquired on a model ferroelectric system, at rates ~500x faster than the current state of the art, with higher spatial and spectral resolution. The obtained results offer a complementary channel of information to supplement existing piezoresponse force microscopy studies, allowing to probe disorder at the nanoscale. Bayesian inference further allows quantification of the capacitance contribution, which can be utilized to estimate the dielectric constant of the ferroelectric, with results agreeing with reported values. These studies highlight the utility of both complete information acquisition, and Bayesian inference, in dramatically increasing the acquisition rates of data from SPM.

This research was sponsored by the Division of Materials Sciences and Engineering, BES, DOE (RKV, SVK, SS). This research was conducted and partially supported (SJ) at the Center for Nanophase Materials Sciences, which is a US DOE Office of Science User Facility. Bayesian inference portion was sponsored by the Applied Mathematics Division of ASCR, DOE; in particular under the ACUMEN project (KJHL, RA).

## 2D Materials Focus Topic

### Room 15 - Session 2D+AS+SA+SP-TuM

#### 2D Materials Characterization including Microscopy and Spectroscopy

Moderator: Sara Barja, Materials Physics Center, San Sebastián, Spain

8:00am **2D+AS+SA+SP-TuM-1 Electronic Structure of Oxygen-Intercalated Graphene on Iridium Interface**, *Yi Lin*, Y Li, Columbia University; *J Sadowski*, Brookhaven National Laboratory; *J Dadap*, W Jin, R Osgood, Columbia University; *M Hybertsen*, Brookhaven National Laboratory

We report experimental and theoretical work to understand how oxygen intercalation changes the image potential state and surface state electronic structure in a metal/graphene interface. We use tunable angle-resolved two-photon photoemission spectroscopy to probe the evolution of the electronic band structure of an epitaxially grown monolayer graphene on Ir(111) as it undergoes through a cycle involving oxygen intercalation and deintercalation. Oxygen intercalation is carried out in situ and LEED is used to determine the crystallinity of the interface in the presence or absence of the intercalated oxygen. The image state manifold and its effective mass are examined. The photoemission intensity variation in momentum space and the observation of an oxygen induced state are discussed. Furthermore, a recently proposed effective potential model at the graphene/metal interface is developed further by us to accommodate oxygen intercalation and interpret our experimental electronic structure variation with good agreements.

We acknowledge support from the US Dept. of Energy, Office of Basic Energy Sciences, under Contract Numbers DE-FG 02-04-ER-46157, DE-FG02-90ER14104, and DESC0012704.

8:20am **2D+AS+SA+SP-TuM-2 Graphene Moiré Pattern Ultra-High Resolution Atomic Force Microscopy**, *Gerald Pascual*, B Kim, K Lee, Park Systems Inc.

The ultra-high resolution of AFM was demonstrated in a Graphene/hexagonal Boron Nitride (hBN) sample evaluation conducted by AFM. The sample consisted of hBN substrate overlaid with a Graphene layer and was scanned under ambient air. The purpose of the evaluation was to assess the AFM ability to characterize the topography of the moiré pattern that was created when one layer was set on top of the other and offset by rotation. Using non-contact AFM mode and a standard AFM probe tip, the AFM was able to successfully image the moiré pattern super lattice constant of the sample in scans as large as 500 x 500 nm. In the higher magnification image taken at a scan size of 60 x 60 nm provides the clear evidence that not only are the super lattice constants of the moiré pattern about 15 nm [1] in width, but that the spacing between each striation on the moiré pattern is roughly 4-5 nm in length. Observations of such striations in Graphene/hBN systems have been previously reported [2]. This latter distance is in line with the expected tip radius curvature values for the AFM tip used to acquire all four sets of data.

[1] A. Zandiatashbar, B. Kim, Y. Yoo, and K. Lee, *Microscopy Today* 23(06):26-31 (2015)

[2] P. Gallagher, M. Lee, F. Amet et al., *Nature Comm.* 7 10745 (2016)

8:40am **2D+AS+SA+SP-TuM-3 Surface and Interface Properties of 2D MoS<sub>2</sub> and WS<sub>2</sub> Materials**, *Chia-Seng Chang*, Institute of Physics, Academia Sinica, Taiwan, Republic of China, Taiwan; *Y Lee*, National Tsing-Hua University, Taiwan, Republic of China

**INVITED**

Two dimensional layered transition metal dichalcogenides (2D TMD), such as MX<sub>2</sub> (M = Mo, W and X = S, Se), have offered exciting new physics and chemistry, as well as potential applications in energy harvesting, electronics, and optoelectronics. Surface and interface properties of these 2D materials are fundamental to further advance them on scientific exploration and device fabrication. In this talk, we will demonstrate the growth of various TMD monolayers using ambient-pressure chemical vapor deposition. The quality of a MS<sub>2</sub> monolayer was examined by scanning probe microscopy, electron microscopy, and optical spectroscopy. We will discuss the key issues associated with the surfaces and interfaces of these materials.

9:20am **2D+AS+SA+SP-TuM-5 Spectroscopic Investigation of Plasma-Fluorinated Monolayer Graphene and Application for Gas Sensing**, *Hui Zhang*, Shanghai Institute of Microsystem And Information Technology, China; *J Guo*, Lawrence Berkeley National Laboratory; *X Sun*, Soochow University

A large-area monolayer fluorinated graphene (FG) is synthesized by a controllable SF<sub>6</sub> plasma treatment. The functional groups of FG are elucidated by various spectroscopies, including Raman, X-ray photoemission spectroscopy (XPS) and near edge X-ray absorption fine structure (NEXAFS). Raman results suggest that the defects are introduced into the monolayer graphene during the fluorination process. The fluorine content can be varied by the plasma treatment and can reach the maximum (~24.6 at% F) under 20 s plasma treatment as examined by XPS measurement. The angle dependent NEXAFS reveals that the fluorine atoms interact with the graphene matrix to form the covalent C-F bonds, which are perpendicular to the basal plane of FG. FG is applied as gas sensing material and owns much better performance for ammonia detection compared to the pristine graphene. Based on our DFT simulation results, the fast response/recovery behavior and high sensitivity of the FG gas sensor are attributed to enhanced physical absorption due to the C-F covalent bonds on the surface of FG

9:40am **2D+AS+SA+SP-TuM-6 Photoemission Electron Microscopy as a New Tool to Study the Electronic Properties of 2D Crystals on Silicon Oxide**, *Taisuke Ohta*, M Berg, Sandia National Laboratories, Center for Integrated Nanotechnologies; *C Chan*, Sandia National Laboratories; *K Keyshar*, Rice University; *G Gupta*, University of Louisville; *P Ajayan*, Rice University; *A Mohite*, Los Alamos National Laboratory

The energy positions of the valence and conduction electronic states with respect to the vacuum level are essential parameters to evaluate how the band gaps of semiconductors or Fermi-levels of metals would line up with respect to each other. Defined as an energy separation between the vacuum level and the highest occupied electronic states, the ionization energy is of particular importance for atomically-thin two-dimensional (2D) crystals to predict the performance of their heterostructures useful in high performance electronics and opto-electronics. Ionization energies have been investigated based on theoretical calculations, but to the best of our knowledge, no systematic experimental confirmation is reported for the wide range of 2D crystals despite their importance.

Here, we present a new approach to study the electronic properties of prototypical 2D crystals, graphene, MoS<sub>2</sub>, WS<sub>2</sub>, and MoSe<sub>2</sub> monolayer and multilayer flakes, supported on thick silicon oxide (SiO<sub>2</sub>) film using a photoemission electron microscopy combined with a deep ultraviolet (DUV) illumination. We determine the band alignments of monolayer to multilayer junctions in these four materials, and show that the ionization energy decreases from MoS<sub>2</sub>, WS<sub>2</sub>, to MoSe<sub>2</sub> as predicted by density functional calculations. We postulate that the defects in SiO<sub>2</sub> alleviate the charging of the 2D crystals thanks to the relatively low total photoemission current due to the low energy excitation by the DUV light. This study reveals a new metrology to uncover electronic properties intrinsic to 2D crystals supported on SiO<sub>2</sub> substrates that interact minimally with the overlying 2D crystals.

The PEEM work was performed at the Center for Integrated Nanotechnologies, an Office of Science User Facility (DE-AC04-94AL85000). T. O. is supported by the CINT user program and Sandia LDRD. The work performed by M. B. and C. C. are supported by a U.S. DOE, Office of Energy Efficiency and Renewable Energy SunShot Initiative award for BRIDGE (DE-FOA-0000654 CPS25859). K. K. was supported by the Army Research Office MURI grant W911NF-11-1-0362. A. D. M. is supported by LANL LDRD program. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

11:00am **2D+AS+SA+SP-TuM-10 STM and STS Study of MoS<sub>2</sub>/WS<sub>2</sub> Heterostructures Grown by Chemical Vapor Deposition**, *Fan Zhang*, Virginia Polytechnic Institute and State University; *Z Lu*, Tsinghua University, PR China; *H Zheng*, K Park, Virginia Polytechnic Institute and State University; *L Jiao*, Tsinghua University, PR China; *C Tao*, Virginia Polytechnic Institute and State University

2D materials like atomically thin transition metal dichalcogenides (TMDs) have received tremendous attentions for their unique properties and high potential applications. Recent developments on synthesis of 2D heterostructures through the chemical vapor deposition (CVD) method

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provide an unprecedented opportunity to create and tune the intriguing electronic and optical properties of 2D materials such as engineering the band gaps. These 2D heterostructures have a wide range of applications in electronics and optics, for example, tunneling transistors, single-photon emission devices and photovoltaic devices. To further optimize and design 2D heterostructures, it is essential to investigate the structural and electronic properties at the atomic scale, which is however still lacking.

In this presentation, we will focus on a high-quality MoS<sub>2</sub>/WS<sub>2</sub> heterostructure grown on SiO<sub>2</sub> using the CVD method. Scanning tunneling microscopy (STM) and spectroscopy (STS) were performed to study the morphology and band structures of both MoS<sub>2</sub> monolayer and MoS<sub>2</sub>/WS<sub>2</sub> heterobilayer. Atomically resolved STM images were obtained on the monolayer, heterobilayer and the interface between the monolayer and heterobilayer. The height histograms acquired respectively on the monolayer and the heterobilayer indicate that the heterobilayer is higher than the monolayer with a height difference of 0.85 ± 0.10 nm. The roughness of the monolayer and heterobilayer was for the first time quantified by STM. The root mean square (RMS) roughness of the heterobilayer is 0.253 ± 0.020 nm compared with 0.362 ± 0.031 nm of the monolayer. We also performed STS measurements on the system. Our STS results and density functional theory (DFT) calculations reveal the band gaps of the heterobilayer and the MoS<sub>2</sub> monolayer, which are similar to the previously reported results on MoS<sub>2</sub>/WS<sub>2</sub> heterostructures fabricated through the mechanical exfoliation method.

**11:20am 2D+AS+SA+SP-TuM-11 Determine the Band Alignment of 2D Semiconductor Heterostructures by Photoelectron Spectromicroscopy,** *L Chang*, National Synchrotron Radiation Research Center, Taiwan, Republic of China; *Y Wang, Y Ku*, National Tsing Hua University, Republic of China; *Y Kuo, H Shiu, Chia-Hao Chen*, National Synchrotron Radiation Research Center, Taiwan, Republic of China

Semiconductor heterojunction (HJ) band alignment is the most important factor for the functioning of the HJ-based devices. Therefore, the prediction and determination of the HJ band offset is always a scientifically interesting and technologically important topic. As the 2D materials emerged as the building blocks for the devices with molecular thickness, the determination of band alignment of the van der Waals HJs is becoming a critical issue.

Due to the nature of the molecular thickness and the lack of large area 2D crystal, a microscope with surface sensitivity is an ideal tool to study the fundamental properties of the 2D heterostructures.

In this regard, we have employed a synchrotron radiation based scanning photoelectron spectromicroscopy (SPEM) to study the chemical and electronic structures of the van der Waals HJs, include the single-layer transition metal dichalcogenides, and graphene/GaN HJs. In this presentation, I will report some of the band alignments of these 2D semiconductor heterostructures.

## Scanning Probe Microscopy Focus Topic

### Room 10 - Session SP+AS+MI+NS+SS-TuM

#### Probing Chemical Reactions at the Nanoscale

**Moderators:** Tae-Hwan Kim, Pohang University of Science and Technology, Gang Nguyen, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

**8:00am SP+AS+MI+NS+SS-TuM-1 Single Molecule Junction: Chemical Optimization of Charge Transport through Single Benzene Derivatives,** *Parisa Yasini, S Afsari, P Pikma, E Borquet*, Temple University

Single molecules are possible components of miniaturized electronic devices. Interconversion between states using external stimuli is a convenient way to generate single molecule devices such as switches and sensors. In this study, we have devised an electromechanical single molecule junction where molecular orientation is controlled by the working electrode potential in an electrochemical environment. We used the scanning tunneling microscopy (STM)-break junction method to measure the electrical properties of benzene derivatives, e.g., tetrafluoroterephthalic acid (TFFPA), terephthalic acid (TPA) and trimesic acid (TMA), bridged between two gold electrodes (the conducting substrate and STM tip). At potentials more negative than zero charge potential, direct contact between the  $\pi$ -system of a benzene ring and the Au (111) electrode results in the formation of a highly ordered monolayer and a high conductance of 0.24 G<sub>0</sub>, 0.22 G<sub>0</sub> and 0.15 G<sub>0</sub> are detected for TFFPA, TPA and TMA, respectively. Moving to potentials more positive than

the potential of zero charge triggers an order-disorder transition as revealed by STM. Our results show that charge transport through the  $\pi$  conjugated benzene ring increases by fluorination of TPA and decreases by an addition of a carboxylic acid functional group to the TPA. Accordingly, these results suggest that using functional groups, charge transport can be modified by manipulation of the electronic structure of molecules.

**8:40am SP+AS+MI+NS+SS-TuM-3 How is Armchair Graphene Nanoribbon Oxidized?** *Chuanxu Ma, A Puzetky, A Baddorf*, Oak Ridge National Laboratory; *Z Xiao, W Lu*, North Carolina State University; *K Hong*, Oak Ridge National Laboratory; *J Bernholc*, North Carolina State University; *A Li*, Oak Ridge National Laboratory

The stability of graphene nanoribbons (GNRs) in air is crucial for practical applications. Here we study the temperature stability of the armchair GNR with a width of seven carbon atoms (7-aGNR) after exposed to air. Combining scanning tunneling microscopy, Raman spectroscopy, x-ray photoemission spectroscopy, and first-principles theory calculations, the oxidation of the armchair GNRs is found to start from the edges at about 520 °C, while below 430 °C the edges are unchanged. Two different types of oxygen species are atomically identified, specifically hydroxyl (OH) and atomic oxygen bridging two carbons, both of which are common oxygen forms in oxidized graphitic lattices. The bandgap is significantly reduced from 2.6 eV to 2.3 eV and 1.9 eV in the vicinity of hydroxyl or bridge O, respectively. Our results suggest that the oxidation will greatly affect the transport properties of GNRs. This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

**9:00am SP+AS+MI+NS+SS-TuM-4 Molecular Chessboard Assemblies Sorted by Site-Specific Interactions of Out-of-Plane d-Orbitals with a Semi-metal Template,** *T Jung*, Paul Scherrer Institut (PSI), Switzerland; *A Wäckerlin, S Fatayer, T Nijs, S Nowakowska, S Mousavi, O Popova, Aisha Ahsan*, University of Basel, Switzerland; *C Wäckerlin*, Paul Scherrer Institut (PSI), Switzerland

We present a conceptually new approach for the formation of 2D chessboard patterns of molecules which is, unlike the other approaches, not dependent on the molecules being functionalized for self-assembly. The deposited Phthalocyanines (Pcs) are sorted in alternating sequence into the 2D layer by their site-specific interaction with the native reconstruction of the bismuth thin-film. The square p-(10 x 10) layer of bismuth on Cu(100) is characterized by the periodic arrangement of shallow pockets which are separated by rims and nodes which originate from the limited registry between Bi and Cu(100). The symmetry and the pitch of 1.8 nm of the Bi/Cu(100) substrate matches with the 4-fold symmetry of the Pc molecules and the pitch of a Pc chessboard arrangement.

We attribute the sorting mechanism to the site-specific interactions between the Bi layer and the out-of-plane 3d states of Mn- and CoPc leading to preferred adsorption sites. The 3d states also allow for the identification of the molecular components in the STM data: Mn and CoPc exhibit a bright contrast on the central metal atom, while Cu in CuPc in absence of such a d-state close to E<sub>f</sub> is depicted as a depression.

Due to this characteristic difference in the 3d states, MnPc + CuPc and CoPc + CuPc sort into chessboard arrays. In these arrays, the molecules with out-of-plane 3d states (CoPc and MnPc) adsorb on the Bi-nodes and the one without (CuPc) adsorbs on the Bi-pores. If both molecules have out-of-plane 3d states around the Fermi level (CoPc + MnPc mixture), the selectivity of adsorption is insufficient and no chessboard layer is formed.

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**11:20am SP+AS+MI+NS+SS-TuM-11 Nanoscale Chemical Analysis with Photo-induced Force Microscopy,** *Sung Park*, Molecular Vista, Inc.

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology. Due to the steep dipole-dipole force dependence on the tip-sample gap distance, PiFM

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spectral images have spatial resolution approaching the topographic resolution of AFM, demonstrating sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various organic, inorganic, and low dimensional materials. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

11:40am **SP+AS+MI+NS+SS-TuM-12 STM Studies of the Molecule-2D Heterointerface**, **Andrew Wee**, National University of Singapore, Singapore; *Y Huang*, Institute of Materials Research & Engineering, Singapore; *Y Zheng*, *Z Song*, National University of Singapore, Singapore; *S Quek*, Department of Physics, National University of Singapore, Singapore

## INVITED

We have previously shown that the electronic and chemical properties of graphene can be controllably tuned via molecular functionalization [1]. In this talk, I will focus on our recent work on semiconducting 2D transition metal dichalcogenides (TMDs) with tunable direct bandgaps dependent on the number of atomic layers. We use high resolution scanning tunneling microscopy/spectroscopy (STM/STS) to study the atomic structure, intrinsic electronic properties, and grain boundaries of MoS<sub>2</sub> and WSe<sub>2</sub> layers on HOPG substrates [2,3]. Using PTCDA as a prototype semiconductor organic molecule, we show that a monolayer TMD can effectively screen an organic-inorganic heterointerface [4]. We have also studied how a C<sub>60</sub>F48 molecular acceptor layer on top of a single-layer WSe<sub>2</sub> acts as p-type dopant, and reveal the electronic structure at a prototypical 1D interface between intrinsic and p-doped WSe<sub>2</sub> [5].

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[4] Z.B. Song et al., submitted.

## 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-TuA-1 Atomic Manipulation of Atomic Oxygen on Graphene, *H Kim, T Ahn, T Youn, D 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-TuA-2 Revealing Distance-Dependence of Chemical Interactions and Image Contrast Reversal in Noncontact Atomic Force Microscopy: A Case Study on Highly Oriented Pyrolytic Graphite, *O Dagdeviren<sup>1</sup>, J Goetzen, E Altman, Udo D. 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

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#### 3:00pm SP+AS+MI+NS+SS-TuA-3 Absence of a Band Gap at Metal-Monolayer MoS<sub>2</sub> Interface, *Abhay Pasupathy*, Columbia University INVITED

**Abstract:** High quality electrical contact to semiconducting transition metal dichalcogenides (TMDCs) such as MoS<sub>2</sub> 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<sub>2</sub> 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<sub>2</sub> within 2 nm of the metal-semiconductor interface. Their decay lengths extend from a minimum of  $\sim 0.55$  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-TuA-7 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<sup>+</sup>-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 1.5x1.5 $\mu\text{m}^2$  square area with a resolution of 30x30 pixels and analyzed using the proposed local DLTS method.

By analyzing the acquired images, time-constant  $\tau$  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  $\tau = 0.3 \mu\text{s}$  and  $3 \mu\text{s}$  were imaged for all samples. The time constants 0.3  $\mu\text{s}$  and 3  $\mu\text{s}$  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-TuA-8 Quantum State Readout of Individual Quantum Dots by Electrostatic Force Detection, *Yoichi Miyahara, A Roy-Gobeil, P 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



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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 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-TuA-9 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-built 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.

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5:20pm **SP+AS+MI+NS+SS-TuA-10 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 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 GaCl<sub>4</sub> (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-TuA-11 Breaking the Time Barrier in Scanning Probe Force Microscopy: Fast Free Force Reconstruction (F<sup>3</sup>R) for Non-contact SPM, L Collins, Stephen Jesse, S 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 (F<sup>3</sup>R)[1] utilizing big data capture and analytics. F<sup>3</sup>R-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.

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6:00pm **SP+AS+MI+NS+SS-TuA-12 Ultrafast G Mode-Kelvin Probe Force Microscopy and its application to probing ionic transport mechanisms in perovskite solar cells., Liam Collins, S Jesse, S 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

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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  $<20 \mu\text{s}$  time resolution and  $\sim 10\text{s nm}$  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.

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# Tuesday Evening Poster Sessions, October 31, 2017

## Scanning Probe Microscopy Focus Topic

### Room Central Hall - Session SP-TuP

#### Scanning Probe Microscopy Poster Session

**SP-TuP-1 Pycroscopy – A Community-Driven Software Package for Analyzing Microscopy Data**, *S Somnath, Chris Smith, S Jesse, R Vasudevan, N Laanait*, Oak Ridge National Laboratory

Microscopy and material science are undergoing profound changes, driven by experimental datasets that are rapidly growing in dimensionality and size, increased accessibility to high-performance computing (HPC) resources, and more sophisticated computer algorithms than ever before. These changes are most pronounced in the functional imaging of materials. However, the softwares supplied with instruments such as microscopes are typically very expensive, do not provide access to advanced or user-defined data analysis routines, and store data in proprietary formats. Furthermore, these proprietary software and data formats not only impede data analysis but also hinder continued research and instrument development, especially in the age of “big data”. Therefore, moving to the forefront of data-intensive materials research requires general and unified data curation and analysis platforms that are community driven and HPC-ready.

We have developed a platform called Pycroscopy that uses community-driven approaches for analyzing and storing data. Pycroscopy is freely available via popular software repositories, and therefore lifts any financial burden for handling data. Pycroscopy uses an intuitive data structure stores data in and hierarchical data format (HDF) files that can be interrogated using any programming language, scales well from kilobyte to terabyte sized datasets, and can readily be used in HPC environments unlike proprietary data formats. More crucially, Pycroscopy uses a universal data format that is curation-ready and therefore both meets the guidelines for data sharing issued to federally funded agencies and satisfies the implementation of digital data management as outlined by the United States Department of Energy. This instrument-independent data format has also greatly simplified the correlation of data acquired from multiple instruments, necessary for comprehensive studies of materials. Unlike many other open-source packages that focus on analytical or processing routines specific to an instrument, the general definition of the Pycroscopy data format can be readily adopted for different microscopy techniques. Furthermore, the generality of Pycroscopy provides material scientists access to a vast and growing library of community-driven data processing and analysis routines that far exceed those provided by instrument manufacturers and are desperately needed in the age of big data. In summary, Pycroscopy can greatly accelerate materials research and discovery through the realms of big, deep, and smart data.

## Scanning Probe Microscopy Focus Topic

### Room 10 - Session SP+SS+TF-WeM

#### Probing and Manipulating Nanoscale Structure

**Moderators:** Zheng Gai, Oak Ridge National Laboratory, Qiang Zou, Oak Ridge National Laboratory

8:00am **SP+SS+TF-WeM-1 STM-Based Nanofabrication and Integrating Nanostructures with Clean Semiconductor Surfaces, Joseph Lyding**, University of Illinois at Urbana-Champaign **INVITED**

Integrating 1D and 2D nanostructures with clean silicon and III-V semiconductor surfaces represents an interesting route towards future hybrid electronic systems. In this effort, we are exploring the integration of carbon nanotubes, graphene and graphene nanoribbons (GNRs) with clean semiconductor surfaces. A key challenge is the fabrication of 'clean' nanostructure-substrate systems. We have addressed this by developing a simple dry contact transfer (DCT) process that enables the deposition of nanostructures onto atomically clean surfaces in ultrahigh vacuum. STM imaging and spectroscopy, coupled with our atomic resolution STM-based hydrogen resist process have been used to study the interactions of carbon nanotubes, graphene and atomically precise graphene nanoribbons with silicon, GaAs and InAs substrates. In these experiments, we have observed the metallic zigzag edge state in graphene<sup>1</sup>, carbon nanotube-substrate lattice alignment effects<sup>2</sup>, and the electronic structure of GNRs<sup>3</sup>. This talk will also show a method for creating sub-5nm metal wires for contacting nanostructures<sup>4</sup>, a SPM probe sharpening technique for producing 1 nm radii probes<sup>5</sup>, and a technique for improving the electronic performance of carbon nanotube array transistors as well as the structural and thermal performance of CNT-based composite materials<sup>6</sup>.

References:

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2. Ruppalt, L.; Lyding, J., Charge transfer between semiconducting carbon nanotubes and their doped GaAs(110) and InAs(110) substrates detected by scanning tunnelling spectroscopy. *Nanotechnology* **2007**, *18* (21).
3. Radocea, A.; Sun, T.; Vo, T.; Sinitskii, A.; Aluru, N.; Lyding, J., Solution-Synthesized Chevron Graphene Nanoribbons Exfoliated onto H:Si(100). *Nano Letters* **2017**, *17* (1), 170-178.
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6. Do, J.; Estrada, D.; Xie, X.; Chang, N.; Mallek, J.; Girolami, G.; Rogers, J.; Pop, E.; Lyding, J., Nanosoldering Carbon Nanotube Junctions by Local Chemical Vapor Deposition for Improved Device Performance. *Nano Letters* **2013**, *13* (12), 5844-5850.

8:40am **SP+SS+TF-WeM-3 Calcium Mediates Adhesion in Reservoir Fluids, S Eichmann**, Aramco Research Center - Boston; **Nancy Burnham**, Worcester Polytechnic Institute

Oil powers modern economies [1]. Yet only 30% of oil is recovered from a typical reservoir [2]. The reservoirs of Saudi Arabia, which provide over 10% of the world's oil [3], are unusual. They are highly saline, with concentrations of up to 120,000 ppm total dissolved solids (TDS), the temperatures can exceed 100° C, and the emulsion of oil and brine is dispersed within small fissures in carbonate rock. These conditions are challenging for the unhindered diffusion of the nanoparticle tracers that are used to map an oil field from one well to the next [4]. In this study, bare and carboxyl-terminated atomic-force microscope tips and calcite surfaces acted as surrogates for nanoparticle tracers and carbonate rocks, respectively. They were immersed in three fluids: brine (120K ppm TDS), seawater (60K ppm TDS), and calcium-doped seawater (~60K ppm TDS). Surprisingly, the amount of total dissolved solids was not a good predictor of the tip-sample adhesion. Rather, specific ion effects were important; adding calcium to seawater brought the adhesion down to the ~100 pN levels of brine as compared to the ~400 pN levels of seawater. The adhesion for the carboxyl-terminated tips was greater (reaching into the nN-range) than for the bare tips, but the same trends were observed.

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These results can be used where fresh water for oil recovery is in short supply. The addition of calcium to seawater should mitigate nanoparticle-rock adhesion and allow more efficient diffusion of nanoparticle tracers through a reservoir, which could in turn lead to better oil recovery and help ensure a stable supply of an essential global resource.

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9:00am **SP+SS+TF-WeM-4 Nanoscopy of Muscovite Mica, Sampath Gamage, M Howard, A Fali**, Georgia State University; **K Bolotin**, Free University of Berlin, Germany; **Y Abate**, Georgia State University

Muscovite type mica is an inorganic material most commonly used as in various electronic devices. Mica also satisfies many characteristics such as excellent thermal stability, high dielectric strength, larger dielectric constant, high Q factor, and high electrical resistivity needed for organic field effect transistors (OFETs) 1-2. We use the near-field imaging and nano-FTIR techniques to investigate nanoscale absorption properties of mica exfoliated on SiO<sub>2</sub> substrate in the frequency range of 4 – 15  $\mu$ m.

References

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2. Lu, X. F.; Majewski, L. A.; Song, A. M., Electrical characterization of mica as an insulator for organic field-effect transistors. *Organic Electronics* **2008**, *9* (4), 473-480.

11:00am **SP+SS+TF-WeM-10 Investigation of Energy Transfer and Conversion at a Single Molecule with an STM, Yousoo Kim**, RIKEN, Japan **INVITED**

Excitation of molecules by light irradiation triggers various important processes including luminescence, photovoltaic effect and photochemical reactions, and detailed understanding of the molecular excited states is crucial to improve organic opto-electronic devices. Absorption spectroscopy is a powerful tool to describe the molecular excitations and the combination with emission (luminescence) spectroscopy which deals with deexcitation processes is effective to investigate the excited states. Single-molecule luminescence detection has progressed rapidly and become indispensable in quantum physics, physical chemistry, and biophysics. However, despite considerable effort and progress, absorption spectroscopy is far behind; number of molecules are still necessary to obtain an absorption spectrum. A difficulty lies in the difference between the diffraction limit of excitation light and absorption cross section of a single molecule.

Here I introduce our recent progresses in measurement of luminescence and absorption spectra and in plasmon-induced reaction at a single-molecule level using a scanning tunnelling microscope equipped with optical detection/excitation facilities.

## Electronic Materials and Photonics Division Room 14 - Session EM+MI+NS+SP+SS-ThM

### Photonics, Optoelectronics, and Light Manipulation

**Moderators:** Yohannes Abate, Georgia State University, Nikolaus Dietz, Georgia State University

#### 8:00am EM+MI+NS+SP+SS-ThM-1 Evolutionary Design of Multi-functional Optical Metasurfaces, *Teri Odom*, Northwestern University **INVITED**

Metasurfaces are an emerging class of flat optics that can manipulate light via subwavelength phase elements. Their 2D structures are usually determined by (1) calculating the phase change required at each location to obtain far-field properties from analytical equations and (2) structuring each building block to produce that wavefront change. However, computational or digital approaches to design metasurfaces based on search heuristics offer advantages in targeting and realizing properties not possible by analytical expressions. This talk will describe an evolutionary approach to design flat lenses based on subwavelength plasmonic building blocks. Our lattice evolution algorithm can achieve desired optical responses by tuning the arrangement of the phase units on a discrete square lattice. We will discuss two different systems with different classes of building units—holes and particles—to realize achromatic flat lenses at up to three wavelengths and flat lenses in semiconductor plasmonic materials such as titanium nitride. We will describe prospects for scaling the production of these lenses as well as their ability to achieve dynamic optical responses.

#### 8:40am EM+MI+NS+SP+SS-ThM-3 Dielectric Freeform Metasurfaces for Optical Sensing, *Arka Majumdar*, University of Washington, Seattle **INVITED**

The macroscopic volume of optical sensors, such as cameras, often originates from the requirement of having multiple optical elements and thick spherical geometries. In recent years, researchers have made subwavelength optical elements, commonly known as metasurfaces, with an ultra-thin form factor using well-developed semiconductor nanofabrication technology. In parallel with the progress in such nano-photonics devices, researchers have also made vast improvements in the field of freeform optics. Freeform optics aim to expand the toolkit of optical elements beyond those exhibiting rotational symmetry. Most conventional optical elements have rotational symmetry for manufacturing reasons, but freeform optics emphasizes complex surface geometries, which are difficult to manufacture by traditional means. While both metasurface and freeform optics have progressed substantially in recent years, they have developed independently of one another as their respective research communities are disconnected.

In our work, we demonstrated how metasurface technology can be used for the realization of subwavelength scale freeform optics, with applications in implantable bio-sensing and potentially in augmented reality systems. I will present some of our recent results on metasurface freeform optics that enable a large depth of focus and a tunable focal length lens. I will also show how these metasurfaces can be used to perform truly colored imaging, by virtue of the extended depth of focus. Finally, I will talk about our ongoing work on metasurface based cavity engineering.

#### 9:20am EM+MI+NS+SP+SS-ThM-5 Moth eye-based, graded index surface treatments to control reflection and light extraction, *L Chan, C Pynn, P Shapturenka, R Ley, S Denbaars, D Morse, Michael Gordon*, University of California at Santa Barbara

This talk will highlight our recent work on bio-inspired surface treatments to control reflection and enhance light extraction at interfaces. An easy, scalable and defect-tolerant surface modification protocol, based on colloidal lithography and plasma etching, was developed to create synthetic 'moth-eye' (ME) anti-reflective structures in different material platforms for photonics and energy applications. Large increases in transmission, bandwidth, and omni-directional response were obtained in Si, Ge, GaAs, ZnS/ZnSe, and CdTe platforms for IR (2-50+  $\mu\text{m}$ ), with performance better than commercial, interference-based coatings. Effective medium theory, finite difference time domain (FDTD) simulations, and quantitative measurements of transmission, reflection and diffuse scattering were used to understand the 'photon balance' of ME films to investigate how optical behavior depends on moth-eye geometry, (dis)order, and pattern fidelity. ME coatings were also implemented in blue-green InGaN/GaN quantum well LED structures on c-plane and semi-

polar substrates to enhance light extraction and device efficiency. A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) compared to a flat surface was achieved using a feature pitch of 2530 nm—performance on par with current photoelectrochemical (PEC) roughening methods. The colloidal lithography roughening technique presented herein is independent of GaN crystal orientation and is therefore applicable to roughening semipolar and nonpolar GaN devices, on which PEC roughening is ineffective.

#### 9:40am EM+MI+NS+SP+SS-ThM-6 Infrared Surface Plasmon-influenced Interfacial Chemistry of Semiconductor Nanocrystals, *W Hu, Michael Filler*, Georgia Institute of Technology

Localized surface plasmon resonances (LSPRs) present exciting opportunities to improve the spatial and temporal control of chemistry at semiconductor surfaces. While the ultraviolet and visible LSPRs supported by metallic nanoparticles are known to impact surface chemistry, heavily-doped semiconductor nanocrystals promise similar capabilities in the near and mid-infrared. Here, we use time-resolved *in situ* infrared spectroscopy to study the influence of mid-infrared LSPRs on a model interfacial process: desorption. We find that the molecular desorption rate for a range of "beacon" molecules (e.g., indole, benzoic acid) on indium tin oxide (ITO) nanocrystals is enhanced by as much as 2x upon illumination with mid-infrared light ( $\sim 0.6\text{-}0.1\text{ eV}$ ) at room temperature. The desorption rate is linearly dependent on light intensity, indicating a single photon process. Experiments as a function of LSPR energy, nanocrystal film thickness, and adsorbate concentration provide clues as to the mechanism of the enhancement. Our findings open new avenues to leverage low energy photons for manipulating chemical reactions on the surfaces of heavily-doped semiconductors.

#### 11:00am EM+MI+NS+SP+SS-ThM-10 Dynamically Tunable Polarization Response in a Si/Au Metamaterial, *Nicole Pfeister*, Tufts University; *C Shemelya*, Technische Universität Kaiserslautern, Germany; *D DeMeo, E Carlson, T Vandervelde*, Tufts University

Polarimetry is utilized across many fields, from chemical characterization to classification of astronomical objects to the detection of man-made items. Present technology requires a different filter for each polarization of light you wish to measure. This requires either a cluster of four pixels to differentiate between the polarizations incident on an area, reducing the final image resolution compared to a non-polarized image, or a filter wheel that adds weight and mechanical reliability issues. Metamaterials can be leveraged to design materials with a polarization sensitive response. Application of a bias voltage can further alter the material's interaction with incident light, resulting in a metamaterial whose response can be tuned dynamically. This technique can be used to create a filter that can be turned on and off for a given polarization. An integrated stack of these filters would allow the measurement of any polarization direction at the full resolution capacity of the detector with the advantages of on-chip integration.

We designed a metamaterial structure that generates a polarization-dependent response in the mid-infrared wavelength range. Off-setting the absorption and transmission peaks for the two polarizations allows equal transmission while the filter is in a static state, or without a bias voltage. The application of a bias changes the metamaterial response and blocks polarized waves parallel to one axis. A thin film semiconductor layer is required to achieve this effect. Previous work utilized thin film gallium arsenide, but poor film quality of the epitaxial layer, with surface roughness on the order of the metamaterial feature size, did not provide sufficient conductivity for an applied bias to impact the light interactions. We will present new results using thin film silicon with a gold nanostructure pattern. A static filter, one that does not require an applied voltage to operate as a polarizing filter, was fabricated to demonstrate the design suitability. We will report on our progress toward a dynamic filter and compare to previous results with III-V films.

#### 11:20am EM+MI+NS+SP+SS-ThM-11 Imaging Stress Induced Lateral Quantum Barrier Manipulation of Indium Gallium Arsenide Quantum Wells, using Micro-Photoluminescence Spectroscopy, *Brian Rummel, M Rimada, S Addamane, G Balakrishnan*, University of New Mexico; *T Sinno*, University of Pennsylvania; *S Han*, University of New Mexico

We have previously demonstrated that a patterned elastic stress field can be used to change the near-surface atomic composition in epitaxial compound semiconductor films.<sup>1</sup> This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner, completely eliminating the need for Stranski-Krastanov growth. For the proof-of-concept, the said mechanism was used to diffuse Ge in a SiGe

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substrate to form regions of Ge-depleted, pure Si surrounded by SiGe. This result opened the door to thermo-mechanically triggered, rewritable circuitry for a wide variety of applications. For the current effort on InGaAs quantum well systems, an array of Si pillars is pressed against a GaAs/In<sub>0.20</sub>Ga<sub>0.80</sub>As/GaAs substrate in a mechanical press, and the assembly is heated to elevated temperatures. The applied elastic stress field promotes the diffusion of larger In atoms away from the compressed regions, leaving In-depleted GaAs in localized regions of the quantum well. Careful assembly and design of the Si nanopillar array would controllably define GaAs and InGaAs regions, producing laterally organized quantum structures. Photoluminescence spectroscopy is used to confirm the diffusion of In and compositional variation, based on the wavelength shift of the emission line from the InGaAs quantum well. In this presentation, we will further discuss how micro-photoluminescence imaging can be used to directly image regions of In-enriched regions as well as In-depleted regions found under the elastically compressed areas. This method may allow us to register the compositionally altered regions for addressable circuitry.

<sup>1</sup> S. Ghosh, D. Kaiser, J. Bonilla, T. Sinno, and S. M. Han, "Stress-Directed Compositional Patterning of SiGe Substrates for Lateral Quantum Barrier Manipulation," *Appl. Phys. Lett.* **107**, 072106-1:5 (2015).

11:40am **EM+MI+NS+SP+SS-ThM-12 Silicon-Based Infrared Photodetectors Enabled by Hot Electrons, Seok-Jun Han, S Han, S Han, University of New Mexico**

Infrared (IR) detectors typically employ low band gap materials, such as InGaAs, InSb, or HgCdTe. However, these materials include elements that are rare, expensive, or toxic. Past research indicates that low-cost, abundant crystalline Si (c-Si) could be used for IR detection when metal electrodes are appropriately nanostructured. In this type of photodetection, the IR with energies below the Si band gap is strongly absorbed by the metal structures. The photoexcited electrons in the metal can then be injected into the conduction band of c-Si before being thermalized, and electric current can be generated. These non-thermalized hot electrons enable the detection of IR light with energies below the c-Si band gap. For efficient transport of electrons in the metal before thermalization, the metal layer should be as thin as approximately the electron mean free path. To induce strong optical absorption in such a thin metal layer, surface plasmon polaritons (SPPs) can be excited at the metal surface. Previous studies on hot electron photodetection utilized small-scale metamaterials or deep trench resonators to have strong resonant absorption of SPPs in thin metal films on c-Si at the desired frequencies. However, these structures had to be fabricated with high precision (e.g., e-beam lithography) because the metal structure size determines resonance. In this study, we pursue a low-cost, manufacturable path, which can tolerate practical fabrication errors. We make use of metal metasurfaces that can be fabricated by scalable, inexpensive techniques and achieve a broad-band IR absorption of over 95% in 15-nm-thick metal films. This unprecedented strong and broad-band absorption is enabled by a new scheme which uses multiple modes of SPPs while the light takes multiple passes within the c-Si substrate. During the passage, light is preferentially absorbed by the thin metal layer that is on one side of the substrate. Absorption on the other side is efficiently eliminated by using a dielectric layer. In our effort, the surface of the c-Si substrate where thin metal film is deposited is structured by a simple optical lithography. The structured surface admits the incident light into the substrate and prevents the light from leaking out of the substrate. In our scheme of multiple light passes, extremely strong resonances are not necessary and fabrication errors would not destroy the optical properties appreciably. In this talk, we will discuss the details of the optical absorption in our scheme. We will also present our experimental results on the electronic characteristics of our hot electron devices.

12:00pm **EM+MI+NS+SP+SS-ThM-13 Low Temperature Wafer Bonding of LTG-GaAs to Si3N4 for Terahertz Photoconductive Switch Application, X Fu, Illinois Institute of Technology and Argonne National Laboratory; M Haji-Sheikh, G Westberg, S Ross, Northern Illinois University; E Landahl, DePaul University; K Attenkofer, Brookhaven National Laboratory; Thomas Wong, Illinois Institute of Technology**

Integrating GaAs optoelectronic devices with Si-based platforms has attracted much attention and efforts in recent years, as a thin layer of GaAs can exhibit superior bulk quality. Wafer bonding, an emerging approach of monolithic integration of GaAs on Si-based substrate, overcomes the lattice mismatch in heterogeneous growth. Several techniques with a post-bonding annealing at temperature exceeding 800°C have been demonstrated to achieve high-energy covalent bonds between III-V

compound semiconductors and Si/SiO<sub>2</sub> systems. However, the elevated temperature bonding process may create not only an inevitable thermal mismatch barrier but also damage the bonding materials. Thus, there is a need for improved technique to integrate GaAs with silicon based devices.

Low temperature grown (LTG) GaAs, which is typically obtained by molecular beam epitaxy (MBE) at temperatures as low as 200°C, offers very attractive properties such as ultra-short carrier lifetime, high electron mobility and high resistivity. It is very desirable for applications such as ultrafast photoconductive switch, high efficiency solar cells and infrared LEDs. Pioneering work has demonstrated techniques to bond LTG-GaAs to Si/SiO<sub>2</sub> at temperature as low as room temperature by means of plasma activation and by wafer bonding under vacuum. However, very few techniques have been developed to bond LTG-GaAs layer to Si<sub>3</sub>N<sub>4</sub> substrate, mainly because Si<sub>3</sub>N<sub>4</sub> is naturally hydrophobic and bonding has been considered unachievable. The existing Si<sub>3</sub>N<sub>4</sub> bonding techniques employ high temperature fusion of Si<sub>3</sub>N<sub>4</sub> layers or apply a layer of bonding agent such as SiO<sub>2</sub>.

In this paper, we report a room temperature approach to directly bond LTG-GaAs to Si<sub>3</sub>N<sub>4</sub> by activating the surface of Si<sub>3</sub>N<sub>4</sub> using weak HF acid solution. This method can be implemented on Si<sub>3</sub>N<sub>4</sub> deposited over wide temperature range. Procedures to reduce the bonding voids and improve the bond strength are also described. In an application to utilize the developed method, we implemented this approach to fabricate a photoconductive switch on Si<sub>3</sub>N<sub>4</sub> substrate bonded with LTG-GaAs and validated that the bonded LTG-GaAs retained the electro-optical properties. A THz optical cross correlation test showed that the photoconductive switch responded swiftly to a femtosecond Ti:Sapphire laser pulse with a resolution of approximately 0.25ps. This wafer bonding method can be integrated with a wide range of microelectronic device fabrication that requires the bonding of LTG-GaAs layer with Si<sub>3</sub>N<sub>4</sub>.

## 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, Indira Seshadri, IBM Research Division, Albany, NY

8:00am **NS+AS+EM+MI+SP+SS-ThM-1 Characterizing Optoelectronically-Active Molecules via STM Imaging and Advanced Raman Spectroscopy Techniques, J Schultz, P Whiteman, Z Poroch, 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 takes 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<sup>-10</sup> 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-ThM-2 BCC to FCC Phase Transition of Pd<sub>x</sub>Cu<sub>1-x</sub> 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<sub>x</sub>Cu<sub>1-x</sub>, 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<sub>x</sub>Cu<sub>1-x</sub> size and composition spread nanoparticle (SCSNP) libraries. Spatially resolved X-

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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<sub>x</sub>Cu<sub>1-x</sub> 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<sub>x</sub>Cu<sub>1-x</sub> SCSNP library on a Mo substrate was prepared using a rotatable shadow mask deposition tool previously developed by our group. After annealing the Pd<sub>x</sub>Cu<sub>1-x</sub> 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<sub>x</sub>Cu<sub>1-x</sub> 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<sub>x</sub>Cu<sub>1-x</sub> 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<sub>x</sub>Cu<sub>1-x</sub> 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-ThM-3 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-ThM-5 Critical Dimension Metrology by Localization Optical Microscopy, C Copeland, C McGray, J Geist, J Liddle, B 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-ThM-6 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-ThM-10 Ultrafast Optical Response of Graphene/LaAlO<sub>3</sub>/SrTiO<sub>3</sub> Heterostructure, L Chen, E Sutton, J Li, M Huang, J Hsu, B D'Urso, University of Pittsburgh; J Lee, H Lee, C 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 LaAlO<sub>3</sub>/SrTiO<sub>3</sub>, has been shown to exhibit great promise for control and detection of broadband THz emission at extreme nanoscale dimensions<sup>1</sup>. Recently, we have successfully integrated these two platforms: we have created graphene/LaAlO<sub>3</sub>/SrTiO<sub>3</sub> structures with (1) high mobility in the graphene channel<sup>2</sup> and (2) oxide nanostructures patterned directly underneath the graphene layer<sup>3</sup>. 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/LaAlO<sub>3</sub>/SrTiO<sub>3</sub> heterostructures.

We gratefully acknowledge financial support from the following agencies and grants: AFOSR FA9550-12-1-0268 (JL, PRI), AFOSR FA9550-12-1-0342 (CBE), ONR N00014-13-1-0806 (JL, CBE), NSF DMR-1234096 (CBE), ONR N00014-15-1-2847 (JL) and N00014-16-3152 (JL).

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2.G. Jnawali, M. Huang, J.-F. Hsu, H. Lee, J.-W. Lee, P. Irvin, C.-B. Eom, B. D'Urso and J. Levy, *Adv. Mater.* **29**, 1603488 (2016).

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4.C. Cen, S. Thiel, G. Hammerl, C.W. Schneider, K.E. Andersen, C.S. Hellberg, J. Mannhart, J. Levy, *Nature Materials* **7**, 298 (2008).

5.G. Jnawali, L. Chen, M. Huang, H. Lee, S. Ryu, J. P. Podkaminer, C. B. Eom, P. Irvin and J. Levy, *APL* **106**, 211101 (2015).

11:40am **NS+AS+EM+MI+SP+SS-ThM-12 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 Stranick*, NIST; *R Ilic*, *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-ThM-13 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 Thelander*, Lund University, Sweden; *C 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 Zb 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.

[1] E. Hilner et al., *Nano Letters*, **8** (2008) 3978; M. Hjort et al., *ACS Nano* **6**, 9679 (2012)

[2] M. Hjort et al., *Nano Letters*, **13**, 4492 (2013)

[3] M. Hjort et al., *ACS Nano*, **8** (2014) 12346

[4] J. L. Webb, et al *Nano Letters* **15** (2015) 4865

[5] J. L. Webb et al., *Nano Research*, **7** (2014) 877

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



## Nanometer-scale Science and Technology Division Room 19 - Session NS+SP+SS-ThA

### Advances in Scanning Probe Microscopy

**Moderator:** Sergei Kalinin, Oak Ridge National Laboratory

2:20pm **NS+SP+SS-ThA-1 Mapping Stress in Polycrystals with sub-10 nm Spatial Resolution**, *Celia Polop*, Universidad Autónoma de Madrid, Spain; *E Vasco*, *A Perrino*, *R Garcia*, Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

From aircraft to electronic devices, and even in Formula One cars, stress is the main cause of degraded material performance and mechanical failure in applications incorporating thin films and coatings. Over the last two decades, the mechanisms responsible for stress generation during film deposition and processing have generated intense conjecture and scientific activity. However, no consensus has been reached so far. The main difficulty is that current models of stress generation, most of which are atomistic in nature, are only supported by data with at best sub-micron resolutions. For example, techniques such as curvature-based measurements, Raman spectroscopy, and x-ray diffraction cannot reveal the stress distribution in films on nanometer scales.

Here, we present a novel method for mapping the stress at the surface of polycrystals with sub-10 nm spatial resolution. This method consists of transforming elastic modulus maps measured by atomic force microscopy (AFM) techniques, such as force modulation method and bimodal AFM, into stress maps via the local stress-stiffening effect. The validity of this approach is supported by Finite Element Modeling simulations. By applying the method to Au polycrystalline films, we show that the intrinsic stress is heterogeneously distributed along the grain diameter, being concentrated in narrow strips adjacent and parallel to the grain boundaries (not directed inside the grain boundary, as is usually assumed). Stress gradients as intense as 100 MPa/nm are detected in these regions. Note that these gradients, which are undetectable by the standard techniques and tests used for stress analysis, are in the order of magnitude of the mechanical strengths required for many applications. The heterogeneous spatial distribution of the intrinsic stress along the grain diameter is the result of the Mullins-type surface diffusion towards the grain boundaries, and would be the probable cause of the kinetic compression that appears in polycrystals under conditions of high atomic mobility. Consequently, we demonstrate that the nanoscale stress mapping has great potential to disclose the nature and origin of the stress in solids.

[1] C. Polop, E. Vasco, A. P. Perrino and R. Garcia, "Mapping stress in polycrystals with sub-10 nm spatial resolution", submitted.

[2] E. Vasco, C. Polop, "The compressive intrinsic stress in polycrystals is not inside the grain boundary", submitted.

3:00pm **NS+SP+SS-ThA-3 XTIP – A Dedicated Beamline for Synchrotron X-ray Scanning Tunneling Microscopy**, *N Shirato*, *M Fisher*, *R Reininger*, *S Hla*, *Volker Rose*, Argonne National Laboratory

Recently, substantial progress was made on Argonne's Synchrotron X-ray Scanning Tunneling Microscopy (SX-STM) project. In particular, we demonstrated the power of SX-STM for elemental characterization and topography of individual Ni nano-islands on Cu(111) at 2 nm lateral resolution with single atom height sensitivity [1], tested a new probe tip concept based on carbon nanotubes [2], and demonstrated soft x-ray imaging of nanoscale magnetic domains of an iron thin-film by x-ray magnetic circular dichroism (XMCD) contrast [3]. Further substantial advances are expected using the new low temperature (LT) SX-STM system, which has been developed over the last 3 years and is currently under commissioning.

To fully exploit the special capabilities of the new LT x-ray microscope, XTIP, a dedicated beamline for SX-STM is under construction at the Advanced Photon Source. To meet the scientific objective of the nanoscience and nanomagnetism communities most effectively, we are going to build a soft x-ray beamline with full polarization control operating over the 500-1600 eV energy range.

The dedicated XTIP beamline will provide researchers access to a one-of-a-kind instrument. Among the potential breakthroughs are "designer" materials created from controlled assembly of atoms and molecules, and the emergence of entirely new phenomena in chemistry and physics.

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Energy Sciences of the U.S. Department of Energy through Grant SC70705. Use of the Advanced Photon Source and the Center for Nanoscale Materials was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under contract DE-AC02-06CH11357.

[1] N. Shirato et al., Nano Letters 14, 6499 (2014).

[2] H. Yan et al., J. Nanomaterials 2015, 492657 (2015).

[3] A. DiLullo et al., J Synchrotron Rad. 23, 574 (2016).

3:20pm **NS+SP+SS-ThA-4 Kelvin Probe Force Microscopy for High-Resolution Imaging of Hydrogen in Steel Alloys**, *Joy McNamara*, *P Korinko*, *M Morgan*, *A Duncan*, Savannah River National Laboratory

Understanding the mechanism of hydrogen interactions in metals is continually a topic of interest for those exploring the use of hydrogen as an alternative fuel source and for other applications which involve the long term storage of hydrogen. Atomic hydrogen in stainless steel alloys segregates to regions of extended defects, such as grain and phase boundaries, and can cause stress and premature cracking in a process known as hydrogen embrittlement. The presence of hydrogen can have serious consequences on the structural integrity and lifetime of hydrogen containers and piping, making it essential to understand the effect of hydrogen on the microstructural properties of stainless steel alloys. The migration of hydrogen through the crystal structure depends on the diffusion rate and solubility of hydrogen in a given phase which gives rise to varying hydrogen concentrations between phases. Hydrogen segregated at the surface of stainless steel specimens and particularly at defect sites changes the local work function of the material and can be measured by Kelvin probe force microscopy (KPFM). By co-locating the presence of hydrogen with extended defects at the surface using KPFM, it may be possible to predict the long term storage properties of a container. KPFM produces nanoscale surface potential (i.e., voltage) images, and is capable of measuring the local change in work function of materials with very high spatial resolution compared to current methods of optically imaging the microstructures of stainless steel. In this work, stainless steel specimens were fabricated by forging techniques and laser engineered net shaping (LENS), a directed energy deposition method of additive manufacturing, and were hydrogen charged at high pressure and temperature for approximately 2 weeks. The samples were then cut and polished to produce smooth surfaces and were imaged using KPFM. The resulting surface potential images show concentration differences of hydrogen at twin boundaries, phase boundaries and other defects as evidenced by a reduction in the local contact potential difference (CPD). Differences in CPD between the forged and LENS samples were observed and will be discussed. This work has potential to elucidate the effects of hydrogen on stainless steel components.

4:00pm **NS+SP+SS-ThA-6 Video-Rate Atomic Force Microscopy**, *Roger Proksch*, Asylum Research **INVITED**

We present results from a new, video rate AFM (Cypher VRS) capable of imaging delicate samples in air and fluid up to 625 lines/second (or >10 frames per second). This is about 300x faster than typical AFMs and 10x faster than current "fast scanning" AFMs. We will describe the architecture of this new AFM, and demonstrate the advantages of its unique design. Some recent specific examples are shown, including: (1) real time observation of the cleavage of a DNA molecule with the DNase1 enzyme. (2) a variety of high resolution examples including Bacteriorhodopsin molecules, the DNA double helix and single atomic point defects, all acquired at frame rates in excess of 1 frame per second, (3) the self-assembly of type I Collagen molecule into fibrils. Collagen molecules were injected on a bare mica surface and let spontaneously polymerize to form fibrils in a phosphate buffer. The typical banding pattern of 67 nm appeared as early as 1 min after introduction of the molecules, and, finally, (4) the dynamics of CTAB hemi-micelles at the solid-liquid interface (HOPG and aqueous buffer). These long molecules spontaneously form micelles in aqueous solutions and hemicylindrical structures upon adsorption onto HOPG. AFM can image these structures with high resolution but with the VRS the kinetics of the formation can now be followed in real time.

4:40pm **NS+SP+SS-ThA-8 Novel AFM Probes Enable Highly Sensitive Chemical and Thermal Characterisation at the Nano Scale**, *Georg Ramer*, *J Chae*, *S An*, NIST Center for Nanoscale Science and Technology / University of Maryland; *V Aksyuk*, *A Centrone*, NIST Center for Nanoscale Science and Technology

Photothermal induced resonance (PTIR) - a hyphenated technique of optical spectroscopy and scanning probe microscopy - allows to perform

# Thursday Afternoon, November 2, 2017

chemical imaging at nanoscale resolution [1,2]. The signal generation in PTIR consists of illuminating the sample with a pulsed tunable laser and transducing the local thermal expansion using a conventional AFM tip. The rapid expansion of the sample induces a ring down motion in the cantilever with amplitudes proportional to the absorption coefficient. Absorption images can be collected by moving the AFM tip across the sample, local absorption spectra can be collected by keeping the tip still and tuning the laser. PTIR works at ambient conditions and is non-destructive, making for a wide range of possible applications.

PTIR has been successfully applied to range of different samples, from life sciences, to photonics, material science and quality control [1,2]. Recently, PTIR sensitivity down to a monolayer has been demonstrated by using optical field enhancement between a gold tip and gold substrate as well as a mechanical enhancement by resonant excitation of the AFM cantilever.

Here, we present latest advances in improving the sensitivity of PTIR. Our novel AFM tips based on a nanosized picogram scale micromechanical cantilever as a displacement sensor and an optical resonator based near field read out achieve a thermal noise limited deflection measurement in the low fm Hz<sup>-0.5</sup> range. Through the high sensitivity and low noise detection of these new probes we obtain PTIR spectra of monolayer samples with high signal to noise ratio, without the need for optical field enhancement or resonant excitation.

Furthermore, low detection noise across the large bandwidth achieved by these probes enables the direct measurement of the sample thermal expansion dynamics after each laser pulse. Leveraging a simple model, the fitting of the thermal expansion dynamics yields the local thermal conductivity at unprecedented, nanoscale lateral resolution.

1 Centrone, A.: 'Infrared Imaging and Spectroscopy Beyond the Diffraction Limit', Annual Review of Analytical Chemistry, 2015, 8, pp. 101-126

2 Dazzi, A., and Prater, C.B.: 'AFM-IR: Technology and Applications in Nanoscale Infrared Spectroscopy and Chemical Imaging', Chem Rev, 2016

5:00pm **NS+SP+SS-ThA-9 Photoinduced Thermal Desorption Coupled with Atmospheric Pressure Chemical Ionization Mass Spectrometry for Multimodal Imaging**, *Matthias Lorenz*, C Brown, University of Tennessee; R Proksch, M Viani, A Labuda, Oxford Instruments; S Jesse, O Ovchinnikova, Oak Ridge National Laboratory

The key to advancing materials is to understand and control their structure and chemistry. However, thorough chemical characterization is challenging since existing techniques characterize only a few properties of the specimen, thereby necessitating multiple measurement platforms to acquire the necessary information. The multimodal combination of atomic force microscopy (AFM) and mass spectrometry (MS) transcends existing analytical capabilities for nanometer scale spatially resolved correlation of the chemical and physical properties of a sample surface. The combination of AFM and MS using resistively heated cantilever tips for thermal desorption has been demonstrated as a promising pathway for multimodal imaging. However, the nano-TA heated probes limit the ability to carry out more standard AFM measurements such as PFM, KPFM and cAFM. To enable a more general application of chemical imaging into an AFM platform we have developed a novel closed cell sampling on an Oxford Instruments Cypher ES for in situ surface sampling/imaging analysis using photothermal heating of the AFM tip for thermal desorption (TD) coupled to a Thermo Orbitrap Velos Pro with inline ionization by atmospheric pressure chemical ionization (APCI). This approach takes advantage of the blueTherm cantilever heating technology developed by Oxford Instruments for localized thermal desorption, and demonstrates its applicability to multimodal chemical imaging using mass spectrometry. The ability to use photothermal heating of an AFM probe versus conventional resistive heating nano-TA technology opens up the possibility for carrying out multiple AFM measurement approaches on a single AFM cantilever, for a true multimodal imaging approach to link chemical composition with material functionality. We show the use of photothermal heating as a means for thermal desorption surface sampling mass spectrometry. We illustrate the application of the AFM-MS coupling for the analysis of small molecules, i.e. pigment yellow 74 as a test substrate to show 500 nm achievable lateral resolution as well as show the application to pharmaceuticals and polymer films. Additionally, the ability to introduce fast heating rates for the TD through ps laser pulsing reduces the melting of sample material and improves the access to intact molecules.

5:40pm **NS+SP+SS-ThA-11 Synchrotron X-ray Scanning Tunneling Microscopy Investigations of Magnetic and Electronic Properties of Nanoscale Metal-Clusters**, *Hao Chang*, Ohio University and Argonne National Laboratory; N Shirato, M Cummings, Argonne National Laboratory; H Kersell, Ohio University and Argonne National Laboratory; D Rosenmann, J Freeland, V Rose, Argonne National Laboratory; S Hla, Ohio University and Argonne National Laboratory

Synchrotron X-ray scanning tunneling microscope (SX-STM) [1,2] combines two of the most powerful materials characterization techniques, synchrotron X-rays and scanning tunneling microscopy. SX-STM has a great potential revolutionize material characterizations with simultaneous elemental, magnetic and topological contrast down to the atomic scale. Here, we will present our recent SX-STM results of nanoscale materials measured at the Advanced Photon Source of Argonne National Laboratory. Using SX-STM X-rays absorption spectroscopy (XAS) technique, we are able to determine the X-ray absorption cross-section of a single nickel and cobalt nanoclusters on a Cu(111) surface. By employing circular polarized synchrotron X-rays, we are also able to demonstrate X-ray magnetic circular dichroism (XMCD) of the Fe L<sub>2</sub> and L<sub>3</sub> edges of a thin iron film deposited on Cu(111) [3] as well as LSMO/LNO superlattices in room and lower temperatures. Here, polarization dependent x-ray absorption spectra have been obtained through a specially fabricated tip that captures photoelectrons. Unlike conventional spin-polarized STM, x-ray excitations provide magnetic contrast even with a non-magnetic tip. Intensity variations in the photo-excited current indicate chemical variations within a single magnetic Fe domain. Moreover, using a hard X-ray nanoprobe beamline, we have successfully detected element specific X-ray induced electron emissions from a single cobalt nanocluster at room temperature. Here, varying the incident x-ray energy across the Co electron binding K-edge enables the detection of elementally sensitive electrons. As the tip scans across the single Co nanocluster- Au(111) surface boundary, atomic spatial dependent changes in the x-ray absorption cross section are directly measured by taking the x-ray induced current as a function of x-ray energy. In addition to presenting the recent results, we will also discuss potential future research directions using SX-STM.

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[2] N. Shirato, M. Cummings, H. Kersell, Y. Li, B. Stripe, D. Rosenmann, S.-W. Hla, and V. Rose. *Nano Lett.* **14**, 6499-6504 (2014).

[3] A. Dilullo, N. Shirato, M. Cummings, H. Kersell, H. Chang, D. Rosenmann, D. Miller, J.W. Freeland, S.-W. Hla, and V. Rose. *J. Synchrotron. Rad.* **23**, 574-578 (2016).

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