Monday Morning, November 7, 2016

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-MoM

Advances in Scanning Probe Microscopy

Moderators: Saban Hus, Oak Ridge National Laboratory, Chanmin Su, Bruker Nano

8:20am **SP+AS+MI+NS+SS-MoM1 Ultrafast Imaging of Polarization Switching in Ferroelectrics via Complete Information Acquisition in SPM***, **Suhas Somnath**, A. Belianinov, S.V. Kalinin, S. Jesse,* Oak Ridge National Laboratory

SPM imaging can be represented as an information channel between the dynamic processes at the tip-surface junction and the observer. Current SPM techniques use heterodyne detection methods such as lock-in amplifiers which result in significant loss in vital information such as information from higher eigenmodes, mode-mixing, and other non-linear phenomena in the tip-surface interaction. We present a new technique called General-mode (G-mode) where we capture the complete broad-band response of the cantilever at sampling rates of 1-100 MHz. The availability of the complete cantilever response facilitates the application of various physical models as well as multivariate statistical methods to extract information that has been unavailable from current SPM techniques. 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 highly sensitive to the local defects and structural imperfections at the micro and nanometer scale, which have undesirable effects on ferroelectric domains. These considerations necessitated the development of Piezoresponse Force Microscopy (PFM) imaging and spectroscopy techniques to measure and manipulate local polarization states. However, the current state-of-art PFM spectroscopy techniques suffer from serious compromises in the measurement rate, measurement area, voltage and spatial resolutions since they require the combination of a slow (~ 1 sec) switching signal and a fast (~ 1 – 10 msec) measurement signal. Furthermore, these techniques only capture the narrow-band cantilever response. We report on a fundamentally new approach that combines the full cantilever response from G-mode with intelligent signal filtering techniques to directly measure 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. The improved measurement speed enables dense 2D maps of material response with minimal drift in the tip position.

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.

8:40am **SP+AS+MI+NS+SS-MoM2 Development of Synchrotron X-ray Scanning Tunneling Microscopy***, **Nozomi Shirato**,* Center for Nanoscale Materials at Argonne National Laboratory*; H. Chang,* Ohio University*; M. Cummings,* Advanced Photon Source at Argonne National Laboratory*; S.W. Hla,* Center for Nanoscale Materials at Argonne National Laboratory*; V. Rose,* Advanced Photon Source at Argonne National Laboratory

Advancements of scanning probe microscopy have been contributing to broaden fundamental understating of surface physics. By combining high intense X-ray beam as a probe and a functionalized tip as a detector, synchrotron X-ray scanning tunneling microscopy has been developed in Advanced Photon Source at Argonne National Laboratory. The recent studies demonstrated the technique has capabilities to extract chemical information with sensitivity at the atomic limit [1] and localized magnetic contrast by utilizing polarized beams [2]. Furthermore, at Argonne, in order to fully exploit potentials of the microscope, a dedicated beamline is under construction. The soft X-ray beamline has the energy range of 400 to 1600 eV and is equipped with a polarizer and focusing optics. The capabilities of the beamline will benefit the communities to explore chemical, magnetic and electronic properties of materials at atomic resolution.

References

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

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

9:00am **SP+AS+MI+NS+SS-MoM3 Development and Integration of a Universal SPM head: Design Criteria and Challenges***, B. Guenther,* Sigma Surface Science GmbH, Germany*; J. Hilton,* Mantis Deposition*; A. Feltz,* Sigma Surface Science GmbH*; **Andreas Bettac**,* Sigma Surface Science GmbH, Germany

Recently we have developed an SPM microscope head that merges the needs for high resolution STM/QPlus[1]-AFM and at the same time satisfies the requirements for integration into different cryogen environments including tip and sample handling.

The new SPM head was integrated into different platforms, e.g. in a UHV Helium Flow Cryostat system for temperatures <10K and in a ^{3}He Magnet Cryostat UHV system for high magnetic fields (±12T) and temperatures <400mK.

This contribution focuses on design aspects and challenges for the new SPM head with respect to spatial restrictions, sample sizes/standards, QPlus and STM signal shielding as well as on first results (STM, STS and QPlus) obtained with the different instrumental setups.

[1] F. J. Giessibl, Applied Physics Letters 73 (1998) 3956

9:20am **SP+AS+MI+NS+SS-MoM4 How Soft Is a Protein? Stress-Strain Curve of Antibody Pentamers with 5 pN and 50 pm Resolutions***, **Alma Perrino**[*],* Instituto de Ciencia de Materiales de Madrid, CSIC, c/ Sor Juana Ines de la Cruz 3, 28049 Madrid, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC,, Spain

Understanding the mechanical functionalities of complex biological systems requires the measurement of the mechanical compliance of their smallest components. Here, we develop a force microscopy method to quantify the softness of a single antibody pentamer by measuring the stress-strain curve with force and deformation resolutions, respectively, of 5 pN and 50 pm [1]. The curve shows three distinctive regions. For ultrasmall compressive forces (5-75 pN), the protein's central region shows that the strain and stress are proportional (elastic regime). This region has an average Young modulus of 2.5 MPa. For forces between 80 and 220 pN, the stress is roughly proportional to the strain with a Young modulus of 9 MPa. Higher forces lead to irreversible deformations (plastic regime). Full elastic recovery could reach deformations amounting 40% of the protein height. The existence of two different elastic regions is explained in terms of the structure of the antibody central region. The stress-strain curve explains the capability of the antibody to sustain multiple collisions without any loss of biological functionality.

[1] Alma P. Perrino and R.Garcia. How soft is a protein? Stress-Strain curve of antibody pentamers with 5 pN and 50 pm resolutions. *Nanoscale,* 10.1039/C5NR07957H (2016)

9:40am **SP+AS+MI+NS+SS-MoM5 AVS Medard W. Welch Award Talk: Action Spectroscopy: Characterizing Molecules at Surfaces and its Dynamics***, **Maki Kawai**[†],* Institute for Molecular Science, Japan*; Y. Kim,* RIKEN Surface and Interface Science Laboratory, Wako, Saitama, Japan*; K. Motobayashi,* Nagoya Institute of Technology, Japan*; H. Ueba,* Toyama University, Japan **INVITED**

STM is a useful tool for spectroscopy utilizing its ultimate spatial resolution. Electronic and vibrational information that STS and inelastic electron tunneling spectroscopy (IETS) carries is not only the reflection of the static spectroscopic information but also related to dynamical phenomena as motion or reaction of molecules induced by the excitation of molecular states. Action spectroscopy is the method to related the action of molecules induced and is utilized to identify the quantum states of the molecules. Dynamical information includes as how molecular vibrations can couple with the relevant dynamical processes [1,2]. I will present typical eamples of how the fundamental excitation of vibration modes is coupled with chemical reactions at surfaces.

References:

[1] Y. Kim, K. Motobayashi, T. Frederiksen, H. Ueba and Maki Kawai, Profress in Surface Science 90 (2015) 85-143, and the references within.

[2] K. Motobayashi, Y. Kim, M. Ohara, H. Ueba and Maki Kawai, Surf. Sci. 634 (2016) 18-22.

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[*] **NSTD Student Award Finalist**

[†] **Medard W. Welch Award Winner**

10:40am **SP+AS+MI+NS+SS-MoM8 Near-Field Spectroscopy and Imaging of Single Nanoparticles***, **Yohannes Abate**, D. Seidlitz, A. Fali, S. Gamage, V.E. Babicheva, V.S. Yakovlev, M.I. Stockman,* Georgia State University*; R. Collazo, D. Alden,* North Carolina State University*; N. Deitz,* Georgia State University **INVITED**

We investigate nanoscale phase separation on single InGaN QDs and nanostructures by using high-resolution s-SNIN (scattering type scanning near-field infrared nanoscopy) technique in the mid-IR spectral region. We fabricated patterned nanolayers down to few atomic layers thick that allow determination of the near-field infrared response of InGaN/InN/GaN heterostructures quantitatively. We first calibrate the near-field IR amplitude contrast as a function of composition and thickness of the semiconductor nanolayers and QDs. We then use this quantitative leads to identify phase separation in single QDs. An advanced theoretical model is developed to guide the experimental results. Unlike previous models that consider the probe conical tip as approximate point dipoles or spheroids, our model considers the full geometry of the tip and all the sample and substrate layers.

11:20am **SP+AS+MI+NS+SS-MoM10 Atomically-resolved Three-dimensional Structures of Electrolyte Aqueous Solutions near a Solid Surface***, **Daniel Martin-Jimenez**, E. Chacon,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain*; P. Tarazona,* IFIMAC Condensed Matter Physics Center, UAM, Spain*; R. Garcia,* Instituto de Ciencia de Materiales de Madrid, CSIC, Spain

Atomic-resolution three-dimensional images of electrolyte solutions near a mica surface demonstrate the existence of three types of interfacial structures [1-3]. At low concentrations (0.01-1 M), cations are adsorbed onto the mica until charge neutrality is reached. The cation layer is topped by a few hydration layers while anions are excluded from the mica surface [4]. At higher concentrations, the interfacial layer extends several nanometers into the liquid. It involves the alternation of cation and anion planes. Classical Fluid Density Functional calculations show that water molecules are a critical factor for stabilizing the structure of the ordered interfacial layer. The interfacial layer compatibilizes a crystal-like structure with liquid-like ion and solvent mobilities. At saturation, some ions precipitate and small ionic crystals are formed on the mica. The three-dimensional images have been acquired at 300 K.

[1] E. T. Herruzo, H. Asakawa, T. Fukuma, and R. Garcia, *Nanoscale* **5**, 2678-2685 (2013).

[2] K. Kobayashi *et al.The Journal of Chemical Physics* **138**, 184704 (2013)

[3] T. Fukuma *et al.Physical Review B* **92**, 7 (2015).

[4] M. Ricci, P. Spijker and K. Voitchovsky *Nat. Commun.* **5**, 4400 (2014).

11:40am **SP+AS+MI+NS+SS-MoM11 Super-resolution Optical and Chemical Imaging of Organic Thin Films using Tip-enhanced Near-Field Optical Microscopy***, A.L. Heilman, R. Hermann,* ***Michael Gordon****,* University of California at Santa Barbara

Sub-diffraction-limited (super-resolution) optical and chemical characterization of organic surfaces using a custom-built tip-enhanced near-field optical microscope with side-on and attenuated total reflectance (ATR) excitation and collection will be discussed. ATR illumination is combined with an Au optical antenna tip to show that (i) the tip can quantitatively transduce the optical near-field (evanescent waves) above the surface by scattering photons into the far-field, (ii) the ATR geometry enables excitation and characterization of surface plasmon polaritons (SPPs), whose associated optical fields can enhance Raman scattering from coumarin-6 (C6) and copper phthalocyanine (CuPc) films, and (iii) SPPs can be used to plasmonically excite the tip for super-resolution chemical imaging of patterned C6 and CuPc via tip-enhanced Raman spectroscopy (TERS). ATR-illumination TERS is quantitatively compared with the more conventional side-on illumination scheme using both experiment and FDTD optical simulations. In both cases, spatial resolution was better than 40 nm and tip on/tip off Raman enhancement factors were >6500. ATR illumination was shown to provide similar Raman signal levels at lower 'effective' pump powers due to additional optical energy delivered by SPPs to the active region in the tip-surface gap. Additional observations, such as the distance scaling of Raman enhancement and inelastic scattering generated by the plasmonic tip, as well as tip-enhanced photoluminescence imaging of patterned phthalocyanine films at spatial resolutions better than 20-30 nm, will be presented.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+2D+AS+NS+SS-MoA

Probing Topological States And Superconductivity

Moderators: An-Ping Li, Oak Ridge National Laboratory, Chuanxu Ma, Oak Ridge National Laboratory

1:40pm **SP+2D+AS+NS+SS-MoA1 Tuning Dirac States by Strain in Topological Insulators***, **Lian Li,*** University of Wisconsin-Milwaukee **INVITED**

Topological insulators (TIs) are distinguished by their metallic boundary states populated by massless Dirac fermions and bulk topological Z_2 index. Changes in the band topology induced by external variables such as strain, electrical field, and composition thus provide a means to tune the boundary states. As a large spin-orbit coupling is necessary to produce an inverted band gap, most TIs discovered to date are narrow gap semiconductors consisting of heavy elements. These materials typically exhibit layered crystal structure with anisotropic bonding characteristic: strong covalent bonding in-plane and weak van der Waals (vdW) bonding out-of-plane, which has been predicted to facilitate effective strain engineering of their bulk band topology.

In this talk, I will first give an overview of the opportunities and challenges in the epitaxial growth of layered TIs. Using the prototypical 3D TI Bi_2Se_3 as an example, I will show that the characteristic anisotropic bonding facilitates a spiral growth mode on virtually any substrates by molecular beam epitaxy. The coalescence of these spirals results in a high density of grain boundaries that consist of alternating edge dislocation pairs, leading to periodic in-plane stretching and compression. Using scanning tunneling spectroscopy, I will show that this local strain field strongly modifies the Dirac surface states, where in-plane compression expands the vdW gap and destroys the Dirac states.

Next, I will show our recent work on the strain engineering of Dirac edge states of epitaxial Bi bilayer films grown on three different substrates: the (111) surface of 3D TIs Bi_2Se_3, Sb_2Te_3, and Bi_2Te_3. Using scanning tunneling microscopy/spectroscopy, I will show that for moderately strained (<6%) single Bi bilayer on Sb_2Te_3 and Bi_2Te_3, edge states are observed; while on highly compressed single Bi bilayer on Bi_2Se_3 (>8%), edge states are suppressed. These findings, supported by density functional theory calculations, demonstrate the uniform control of edge states in 2D topological insulators by strain.

2:20pm **SP+2D+AS+NS+SS-MoA3 Detection of Current Induced Spin Polarization in Topological Insulators via Four-Probe Spectroscopy***, **Saban Hus,*** Oak Ridge National Laboratory*; Y. Chen,* Purdue University*; A.-P. Li,* Oak Ridge National Laboratory

Charge currents carried by the nontrivial surface states of topological insulators (TIs) exhibit a net spin polarization due to spin-momentum locking. Electrical detection of such a spin polarization is crucial for technological applications. However, in 3D TI materials the existence of a bulk conduction channel makes it difficult to quantify the density and the spin polarization of the current carried by the surface states. Here we report in-situ, spin sensitive four-probe spectroscopy measurements on Bi_2Te_2Se single crystals. A ferromagnetic probe detects the net spin accumulation on the surface states while a set of four-probe spectroscopy measurement is used for a quantitative separation of 2D and 3D conduction. We also examine the effect of surface doping by residual gas molecules on the current induced spin polarization. Even though, the additional carriers by dopants enhance the 2D conductance in TIs they reduce the net spin polarization of current carried by topological surface states.

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

2:40pm **SP+2D+AS+NS+SS-MoA4 Switching Handedness of Chiral Solitons Under Z_4 Topology***, **Tae-Hwan Kim,*** Pohang University of Science and Technology, Republic of Korea*; S. Cheon, H.W. Yeom,* Institute for Basic Science (IBS), Republic of Korea

Chirality is a ubiquitous and interesting property of asymmetry in many fields ranging from biology, chemistry to physics. Because of its topologically distinct nature, such chiral objects in condensed matter are often topologically excited states, which are protected by system's topology and can be used to carry information robustly against external perturbations. For instance, nanoscale magnetic skyrmions, spatially localized chiral spin texture with particle-like properties in ferromagnets, have been investigated intensively as topological information carriers for next generation spintronic devices. However, logic operations using topological excitations such as skyrmions are only conceptually proposed. On the other hand, chiral solitons are recently discovered as the topologically protected edge states of one-dimensional Z_4 topological insulators [1,2], which can be exploited as topological information carriers in electronic system. In this talk, I show experimentally and directly that switching between solitons with different chirality is possible by merging them with achiral solitons [3]. I will also show that this chiral switching corresponds to the realization of topological addition of the Z_4 topological number or chirality. With their distinct topologically protected chirality, chiral solitons could uniquely be applied for robust multilevel information storage and logic operation by storing, carrying, and switching three differently topological bits of information.

[1] T.-H. Kim and H. W. Yeom, Phys. Rev. Lett. **109**, 246802 (2012).

[2] S. Cheon, T.-H. Kim, S.-H. Lee, and H. W. Yeom, Science **350**, 182 (2015).

[3] T.-H. Kim, S. Cheon, and H. W. Yeom, submitted (2016).

3:00pm **SP+2D+AS+NS+SS-MoA5 Spectroscopic-imaging STM Studies on Dirac-Landau Levels in the Topological Surface State***, **Tetsuo Hanaguri,*** RIKEN Center for Emergent Matter Science, Japan **INVITED**

We show that spectroscopic-imaging scanning tunneling microscopy (SI-STM) is a powerful tool to investigate unique electronic features of massless Dirac electrons in a magnetic field.

In contrast to the conventional massive electron that is described by a single-component wave function, the massless counterpart demands the two-component wave function. In the case of the surface state of topological insulators, these two components are associated with the spin degrees of freedom, thereby governing the magnetic properties. Thus, it is highly desirable for spintronics applications to elucidate where and how the two-component nature emerges. We found that the two-component nature manifests itself in the internal structures of Landau orbits. We visualized the local density-of-states (LDOS) distributions associated with the Landau orbits in the topological surface state of Bi_2Se_3 using SI-STM. In the presence of the potential variation, Landau orbits drift along the equipotential lines, forming ring-like patterns in the LDOS images. The observed internal structures of the rings are qualitatively different from those of conventional massive electrons but are well reproduced by the calculation based on a two-component model Dirac Hamiltonian. Our model further predicts non-trivial energy-dependent spin-magnetization textures around the potential minimum. This is originated from the interplay between the two components and may provide a clue to manipulate spins in the topological surface state.

In addition to the Landau orbits, we succeeded in observing the Zeeman shift of the lowest Landau level from which precise g factor of the massless Dirac electron can be estimated. We performed experiments on two topological insulators, Bi_2Se_3 and Sb_2Te_2Se, and determined the surface g factors of them to be 18 and -6, respectively. Such remarkable material dependence suggests that the Zeeman effect is tunable by controlling the chemical composition, providing a new knob in manipulating the spins in the topological surface state.

4:00pm **SP+2D+AS+NS+SS-MoA8 The Rashba and Quantum Size Effects in Ultrathin Bi films***, **Toru Hirahara,*** Tokyo Institue of Technology, Japan **INVITED**

Precise characterization of physical properties in nanometer-scale materials is interesting not only in terms of low-dimensional physics but also in application to devices. Due to the reduced dimensionality and symmetry, these systems possess various interesting properties that cannot be found in the bulk. In this presentation, focusing on epitaxial ultrathin bismuth films formed on a silicon substrate, we introduce an intriguing interplay of the quantum size and Rashba effects in reciprocal space. Utilizing spin- and angle-resolved photoemission spectroscopy, we observed clear Rashba-split nature of the surface-state bands in these Bi films. However, the band dispersion did not follow the simple Rashba picture and the spin-splitting was lost where they overlapped with the bulk projection. From first-principles calculations, this was explained as a change in the nature of the band-splitting into an even-odd splitting induced by the quantum size effect [1]. Furthermore, we show that the interplay of the quantum size effect and the presence of the surface state induces a complicated change in the Fermi level position of the bulk states in bismuth, which is critical in discussing the surface-state contribution in the film properties [2,3].

[1] T. Hirahara, Journal of Electron Spectroscopy and Related Phenomena **201**, 98 (2015).

[2] T. Hirahara, T. Shirai, T. Hajiri, M. Matsunami, K. Tanaka, S. Kimura, S. Hasegawa, and K. Kobayashi, Physical Review Letters **115**, 106803 (2015).

[3] M. Aitani, T. Hirahara, S. Ichinokura, M. Hanaduka, D. Shin, and S. Hasegawa, Physical Review Letters **113**, 206802 (2014).

4:40pm **SP+2D+AS+NS+SS-MoA10 Understanding the Microscopic Effects of Annealing in Ba($Fe_{1-x}Co_x$)$_2$$As_2$ Superconductor***, **Qiang Zou**, Z. Wu, Q. Zheng, S. Rajputł, D.S. Parker, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

By hole or electron doping of the parent iron-based $BaFe_2As_2$ compound, the high-transition temperature superconductivity emerges from the suppression of the antiferromagnetic order.[1] It was widely reported that thermal-annealing significantly improves some superconducting characteristics in Ba($Fe_{1-x}Co_x$)$_2$$As_2$, including T_c[2] The microscopic origin of such effect is still an open question. To make a connection between the global and the microscopic behavior of the materials, we did a comparison measurement on the pair of well-characterized x, we call ' as-grown' vs 'annealed' Ba($Fe_{1-x}Co_x$)$_2$$As_2$ crystals, and using low temperature scanning tunneling microscopy and spectroscopy (STM/S). The superconducting gap maps deducted from the dI/dV maps were compared. The gap width distribution of the as-grown sample are obviously narrower than that of the annealed one. The coherent peak position also shifted to higher value for the annealed sample. The corresponding reduced-gaps of $2\Delta/k_bT_{c1}$ are about 2.3 and 5.4 for the as-grown and annealed crystals, respectively. The difference of the reduced-gaps indicates that the pairing strength of the annealed crystal is stronger than the as-grown one.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division . A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Reference

1. Stewart, G. R. (2011). "Superconductivity in iron compounds", *Reviews of Modern Physics*, *83*(4), 1589.

2. Gofryk, K., et al. "Effect of annealing on the specific heat of Ba($Fe_{1-x}Co_x$)$_2$$As_2$" *Physical Review B, 83(6), 064513*

5:00pm **SP+2D+AS+NS+SS-MoA11 Annealing Effect on the Properties of Superconducting Parent $BaFe_2As_2$ Crystal***, **Shivani Rajput**, Q. Zou, A.S. Sefat, Z. Gai,* Oak Ridge National Laboratory

Understanding of electronic interactions in a parent phase of a superconducting crystal is crucial in determining the mechanism behind high Tc superconductivity. Bulk measurements show that annealing of parent $BaFe_2As_2$ crystal at 700 ^{0}C for 30 days causes a 5 K shift in magnetic transition temperature (T_N) compared to as grown crystal. To understand the effect of annealing and details of magnetic phase transition, we investigate as-grown and annealed $BaFe_2As_2$ crystals at atomic scale using a variable temperature scanning tunneling microscopy/ spectroscopy at various temperature points across T_N. Tunneling spectroscopy exhibit a ~ 0.53 eV gap type feature above T_N, while V-shape dI/dV spectra below T_N. The dI/dV mapping measurements show that as-grown $BaFe_2As_2$ crystals are electronically inhomogeneous, and averaging the differential conductance spectra over a large area does not truly represent the electronic properties of the sample at local scale, whereas annealed sample is comparatively electronically homogeneous.

This research was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Division. A portion of this research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuM

Probing Chemical Reactions at the Nanoscale
Moderator: Tae-Hwan Kim, Pohang University of Science and Technology

8:00am **SP+AS+MI+NS+SS-TuM1 *In Situ* Probing of Oxygen Vacancy Diffusion Across Multilayer Oxide Heterostructures**, *J. Zhu,* University of Massachusetts - Amherst*; J.-W. Lee, H. Lee,* University of Wisconsin - Madison*; R. DeSouza,* RWTH Aachen University, Germany*; C.-B. Eom,* University of Wisconsin - Madison*; **Stephen Nonnenmann,*** University of Massachusetts - Amherst

Complex oxide heterostructures display an extraordinary array of exotic collective and correlated physical phenomena that result from exploiting the strong interplay between structural and electronic degrees of freedom. Oxygen vacancies often facilitate or govern the interfacial phenomenon observed at or across well-defined discrete interfaces, ranging from domain wall pinning within ferroic systems to electron donors in conducting systems. Realization of multifunctionality within oxide heterostructures therefore necessitates a direct, proper understanding of the interrelationship exhibited by concomitant, defect-mediated transport mechanisms with adequate spatial resolution. Here we utilize a modified, *in situ* scanning probe technique to measure the surface potential across a multi-layered yttria-stabilized zirconia / strontium titanate (YSZ/STO) heterostructured film at 500 °C. Subsequent application of a classic semiconductor dopant formalism to the work function profile derived from the surface potential enables mapping of the oxygen vacancy distribution within STO with a resolution < 100 nm. The results presented herein demonstrate the promise of *in situ* scanning surface potential microscopy (SSPM) to investigate complex oxide interfacial systems multilayers that exhibit vacancy-dominated properties, under extreme environmental perturbation, on a highly localized scale.

8:20am **SP+AS+MI+NS+SS-TuM2 Study of Surface Chemistry on Various Noble Metal Surfaces by Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy**, ***Naihao Chiang,*** Northwestern University*; D. Chulhai,* Pennsylvania State University*; G. Goubert, L. Madison, X. Chen, E. Pozzi, M.C. Hersam, T. Seideman,* Northwestern University*; N. Jiang,* University of Illinois at Chicago*; L. Jensen,* Pennsylvania State University*; G. Schatz, R.P. Van Duyne,* Northwestern University

During the last few years, there has been an explosion of interest and activity in the field of nanoscale vibrational spectroscopy. Tip-enhanced Raman spectroscopy (TERS) combines the ability of scanning tunneling microscopy (STM) to resolve atomic scale surface features with the single molecule chemical sensitivity of surface-enhanced Raman spectroscopy (SERS). The goal is to understand and manipulate chemistry on the nanometer length scale using the properties of the collective electronic excitations in noble metal nanostructures, known as localized surface plasmon resonance (LSPR).

Two recent advances in ultrahigh vacuum (UHV) TERS which illustrate the power of this nanoscale vibrational spectroscopy will be presented. First, our current understanding of the adsorbate-surface and adsorbate-plasmon interactions involved in the UHV-TERS of the N-N'-bis(2,6-diisopropylphenyl)-perylene-3,4,9,10-bis(dicarboximide) (PDI) on various single crystal surfaces (Ag(111), Ag(100), Cu(111), and Au(111)) which probed by a Ag tip will be discussed. This study demonstrates that TERS is a substrate general technique. Additionally, the LSPR of the Ag tip-Ag sample junction is as broad as a Ag nanoparticle dimer system. Therefore, TERS on Ag tip-Ag sample systems is also excitation general.

Second, new insights into the nature of a conformational dynamics involved at room temperature will be described. We have interrogated the conformational change of *meso*-tetrakis-(3,5-di-tertiarybutylphenyl)-porphyrin (H_2TBPP) on a Cu(111) surface between two stable conformations. At room temperature, the barrier between the porphyrin ring buckling up/down conformations of the H_2TBPP-Cu(111) system is easily overcome, and our group has achieved unprecedented sub-nm resolution by simultaneous UHV-TERS and STM analysis. This topic illuminates that TERS can unambiguously distinguish the conformational differences between neighboring molecules with single molecule resolution. Furthermore, the sub-nm resolution led to the direct observation of single molecule transitions between states from one scan to the next.

8:40am **SP+AS+MI+NS+SS-TuM3 Exploring Surface-assisted Reactions Toward Functional Carbon Nanostructures**, ***Xiaohui Qiu,*** National Center for Nanoscience and Technology, China **INVITED**

Understanding the dehydrogenation and dehalogenation reactions of molecular entities on surface is essential for the controlled synthesis of carbon-based nanostructures. Delicately designed precursor molecules exploit the potential of selective activation of functional groups and templating effect of substrates and promise the fabrication of nanoscale building blocks with desired geometries. Here we employed a combination of scanning tunneling microscopy, atomic force microscopy, and theoretical calculation to elucidate self-assembling of halogen-containing molecules on metal surfaces. Metallo-supramolecular assemblies are constructed via coordination bonding between metal atoms and halogen ligands. The spontaneously formed molecular scaffolds are further explored to program the structure and chemical composition of hybrid carbon architecture. We reveal the hierarchic reaction pathway of a few aromatic derivatives in an effort toward realizing carbon-based nanostructures with controllable electronic, optical and magnetic properties.

9:20am **SP+AS+MI+NS+SS-TuM5 Landscapes in Conversion of Quasi-Free-Standing Polymer Chains to Graphene Nanoribbons**, ***Chuanxu Ma,*** Oak Ridge National Laboratory*; Z. Xiao,* North Carolina State University*; L. Liang,* Oak Ridge National Laboratory*; W. Lu, J. Bernholc,* North Carolina State University*; K. Hong, B.G. Sumpter, A.-P. Li,* Oak Ridge National Laboratory

Although the cyclodehydrogenation is well known as a key step in the bottom-up preparation of graphene nanoribbons (GNRs), the mechanism is still unclear. To understand and control the cyclodehydrogenation can help to create novel intraribbon heterojunctions of GNR-based structures. Here, we demonstrate the conversion of quasi-free-standing polymer chains to GNRs induced by thermal annealing and manipulations with a scanning tunneling microscope tip. Combined with the density functional theory calculations, a domino-like fashion and the hole-involved cyclodehydrogenation are proposed for the thermal annealing and tip-induced conversion of polymer chains to GNRs, respectively. Our results provide the first direct experimental evidence that the catalytic effect of the Au substrate is critical to the thermal-induced cyclodehydrogenation in forming bottom-up GNRs. Strongly localized density of states in the short GNR segment of the polymer–GNR herterojunction is observed. The significant confinement of the charge carriers is attributed to the big bandgap difference between the two segments of the heterojunction. Our findings might pave new ways to form GNR-based intraribbon heterojunctions by controlling the cyclodehydrogenation during bottom-up preparation, and shed light to the potential applications of the polymer–GNR herterojunctions.

This research was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility, and partially supported by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the US DOE.

11:00am **SP+AS+MI+NS+SS-TuM10 Imaging Single Molecule Chemistry**, ***Wilson Ho,*** University of California Irvine **INVITED**

Single molecule chemistry can now be probed at unprecedented spatial resolution with a low temperature scanning tunneling microscope (STM) in ultrahigh vacuum. Advances in this field have provided new measurements and insights into the structure and function of molecules through real space imaging and high resolution vibrational spectroscopy. The combination of the STM with optical spectroscopy and femtosecond lasers has added a new dimension of time to space and enabled the probing of single molecule dynamics in light-matter interaction with better than 0.1 nm resolution. The ability to visualize single molecule chemistry has reinvigorated the study of molecules and their transformations on solid surfaces. Much of the scientific advancement and understanding in surface chemistry have derived from the well-defined conditions that have long been championed by surface science in providing unambiguous results that are appealing to the theoretical and experimental communities. Imaging single molecule chemistry has a broader impact on general chemistry due principally to direct visualization of molecules and their inner machinery at the limit of space and time.

11:40am **SP+AS+MI+NS+SS-TuM12 Atomic Force Microscopy: A Tool for Chemical Analysis of Surfaces and Molecules on Atomic Scale***, **Pavel Jelinek**,* Institute of Physics of the AS CR, Czech Republic **INVITED**

Atomic resolution and manipulation is routinely achieved by both scanning tunneling microscopy (STM) and atomic force microscopy (AFM) nowadays. Despite of large activities in development of the scanning probe technique, still some challenges remain, namely the chemical analysis on atomic and molecular level.

First, we will present a novel method extending further the chemical analysis [1,2] by means of AFM. Namely we will discuss a new methodology to measure Pauling's electronegativity of individual atoms on surfaces using AFM. Electronegativity has been an important concept in chemistry, originally defined by Pauling as "*the power of an atom in a molecule to attract electrons to itself*". However, its experimental determination on individual surface atoms was not possible so far.

Second, we will discuss the origin of sub molecular AFM/STM resolution acquired with functionalized tips. We will show that the electrostatic force can substantially affect the sub molecular contrast. We will show, that the electrostatic potential on a single molecule can be mapped out with sub molecular resolution.

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Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+AS+MI+NS+SS-TuA

Probing Spin-Dependent Phenomena

Moderators: Phillip First, Georgia Institute of Technology, Shivani Rajput, Oak Ridge National Laboratory

2:20pm **SP+AS+MI+NS+SS-TuA1 Spin Sensing and Magnetic Design at the Single Atom Level**, ***Alexander Khajetoorians,*** Radboud University, The Netherlands **INVITED**

Unraveling many of the current dilemmas in nanoscience hinges on the advancement of techniques which can probe the spin degrees of freedom with high spatial, energy, and ultimately high temporal resolution. With the development of sub-Kelvin high-magnetic field STM, two complementary methods, namely spin-polarized scanning tunneling spectroscopy (SP-STS) [1] and inelastic STS (ISTS) [2-3], can address single spins at the atomic scale with unprecedented precession. While SP-STS reads out the projection of the impurity magnetization, ISTS detects the excitations of this magnetization as a function of an external magnetic field. They are thus the analogs of magnetometry and spin resonance measurements pushed to the single atom limit. We have recently demonstrated that it is possible to reliably combine single atom magnetometry with an atom-by-atom bottom-up fabrication to realize complex atomic-scale magnets with tailored properties [4-6] on metallic surfaces [1,7]. I will discuss the current state of the art of this growing field as it pertains to single spin information storage, and how the functionality of coupled magnetic adatoms can be tailored on surfaces by substrate mediated interactions. I will discuss our recent efforts toward realizing tailored chiral magnets [8] and present an outlook on future perspectives toward probing quantum matter at ultra-low temperatures.

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3:00pm **SP+AS+MI+NS+SS-TuA3 Electron Spin Resonance of Single Atom and Engineered Spin Structures**, ***Taeyoung Choi****, W. Paul, C.P. Lutz, A.J. Heinrich,* IBM Almaden Research Center **INVITED**

The scanning tunneling microscope (STM) has been one of the most versatile tools for atomic-scale imaging, manipulation, and tunneling spectroscopy. Inelastic spin excitation and spin-polarized tunneling have been employed to study spin physics of individual atoms and engineered structures, demonstrating nanoscale memory bits [1] and logic gates [2]. However, the energy resolution of the STM is mainly limited by a temperature of a system surrounding the atomic spins (>100 µeV).

Here, we successfully combine electron spin resonance (ESR) and STM, coherently driving spin resonance of individual iron (Fe) atoms on surfaces (MgO/Ag(100)) [3]. A radio-frequency electric field (~20 GHz), applied at the tunneling junction, modulates the spin state of the Fe atoms. The spin resonance signal is detected by a spin-polarized tunneling current. The ESR signals from individual Fe atoms differ by a few GHz (~10µeV) while the ESR linewidth is in the range of only a few MHz (~10neV). Such a high energy resolution enables us to distinguish spin distributions down to single-atom level and to investigate weak magnetic interactions.

When we placed two Fe atoms close together with controlled atom manipulation, we found that the ESR signal from each Fe atom splits into doublet, of which separation depends on the distance between two atoms. Our measurements show $r^{-3.024\pm0.026}$ distance-dependent splitting, in excellent agreement of magnetic dipole-dipole interaction. We utilized this precisely measured dipolar interaction to determine the location and magnetic moment of unknown spin centers with sub-angstrom and one hundredth of Bohr magneton precision [4].

Coherent quantum control of individual atoms on surfaces combined with atom manipulation may promise the STM as a new and unique platform for a quantum sensor, investigating spin-labeled molecular structures and a quantum information processor, modeling quantum magnetism.

We gratefully acknowledge financial support from the IBM and Office of Naval Research.

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[2] A.A. Khajetoorians, J. Wiebe, B. Chilian, and R. Wiesendanger, Science **332**, 1062 (2011).

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4:40pm **SP+AS+MI+NS+SS-TuA8 Controlling Kondo Effect of Magnetic Molecules on Au(111) by Small Molecule Binding**, ***MinHui Chang****, S.J. Kahng,* Korea University, Republic of Korea*; Y.H. Chang,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea*; H.W. Kim, S.H. Lee,* Korea University, Republic of Korea*; Y.-H. Kim,* KAIST, Republic of Korea

Controlling and sensing spin states of magnetic molecules at the single molecule level is essential for spintronic molecular device applications. Here, we demonstrate that spin interactions of Co-porphyrin on Au(111) can be controlled by adsorption and desorption of small molecules, and be sensed using scanning tunneling microscopy and spectroscopy (STM and STS). Bare Co-porphyrin showed a clear zero-bias peak, a signature of Kondo effect in STS, whereas Co-porphyrin adsorbed small molecules showed modified zero-bias peaks, with reduced full width half maximum or Kondo temperature. Our density functional theory calculation results explain it with spatial redistribution of unpaired spins in d_z2 Orbitals. Our study opens up ways to tune molecular spin interactions by means of chemical binding.

5:00pm **SP+AS+MI+NS+SS-TuA9 Spin-polarized Scanning Tunneling Microscopy on Surfaces Prepared by Molecular Beam Epitaxy**, ***Arthur Smith****,* Ohio University Nanoscale and Quantum Phenomena Institute **INVITED**

Spin-polarized scanning tunneling microscopy (SP-STM) has proven to be a powerful *in-situ* technique for obtaining detailed information about spin structures at surfaces down to atomic scale.[1] It has been applied extensively to investigate pristine ferromagnetic and antiferromagnetic (aFM) transition metal surfaces, with many great results in the case of model systems such as nano-sized magnetic islands and single magnetic monolayers.[2] This has led to fascinating discoveries of nanoscale magnetic domains, domain walls, spin spirals, spin skyrmions, and much more.[3,4] Although not simple in practice, SP-STM can in principle also yield unprecedented spin characterization on a broad spectrum of material surfaces, including practical, real world systems. For example, it could be applied to investigate surfaces of intermetallic compounds, superconductors, complex magnetic oxides, and magnetic semiconductors.

We are applying SP-STM to study various magnetic systems grown *in-situ* by molecular beam epitaxy, including transition metal nitrides,[5] magnetic-doped nitride semiconductors, and several bi-metallic magnetic systems. I will present our recent work using STM and SP-STM, beginning with a discussion of manganese nitrides, including our work on aFM θ-phase MnN and ferrimagnetic ε-phase Mn_4N. The θ-phase films are very complex due to the expectation of canted spins within each atomic layer with four unique canting angles, while the ε-phase films contain two types of spins (Mn^I and Mn^{II}) with equally complex spin arrangements.

A second material we are working on is the chromium nitride system in which we investigate its electronic and spin properties in a low-temperature SP-STM system. Spectroscopy results to date suggest a *d*-wave resonance on the surface and a Kondo signature for nanoscale iron islands grown on atomically-smooth CrN surfaces.

I will also present results for Mn δ-doped semiconducting gallium nitride surfaces in which we find atomic layer ferromagnetism within a unique and stable √3 x √3 - R30° MnGaN surface reconstruction. Spectroscopy clearly reveals spin-polarized and spin-split Mn states, as predicted by first principles theory calculations. SP-STM measurements map out ferromagnetic domains at *room temperature*, and the additional presence of magnetic rim states seen at the edges of ferromagnetic islands, as well as magnetic hysteresis, give further interest to this intriguing system.

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5:40pm **SP+AS+MI+NS+SS-TuA11 The Use of Scanning Probe Techniques to Study the Behaviour of Second Phase Particles in Beryllium and Their Role in Localised Corrosion***, **Christopher Mallinson**, J.F. Watts,* University of Surrey, UK

Scanning Kelvin probe force microscopy (SKPFM) has been employed to examine the galvanic activity of a wide range of second phase particles in S-65 beryllium that are believed to have a role in the localised corrosion of the metal. SKPFM and AFM analysis has been combined with additional surface and bulk analysis techniques of scanning electron microscopy, energy dispersive x-ray spectroscopy and Auger electron spectroscopy to provide a detailed overview of the link between the bulk and surface composition of particles and their Volta potential or surface contact potential.

Initial results appear to show that all second phase particles are more noble than the beryllium matrix with the greatest potential difference observed for $AlFeBe_4$ and alumina or carbide like particles. The more negative Volta potential indicates that the particles should act as local cathodes when the metal is exposed to an aqueous environment.

The initial investigation, which is being performed in-air, will be expanded to determine the effect of increasingly higher humidity environments on the behaviour of the particles. It is hoped that this will provide a greater understanding about the onset of pitting corrosion in beryllium.

6:00pm **SP+AS+MI+NS+SS-TuA12 Many-body Interaction induced Spin-split States of Single Vacancy in Graphite***, **Wonhee Ko**,* Samsung Advanced Institute of Technology, Republic of Korea*; H.W. Kim, Y. Cho,* Samsung Advanced Institute of Technology*; Y. Kuk,* Seoul National University, Korea, Republic of Korea*; S.W. Hwang,* Samsung Advanced Institute of Technology

Although carbon atoms have no magnetic states, it has been known that defects in graphene or graphite can have magnetic states induced by many-body interaction. By utilizing ultra-low-temperature scanning tunneling microscopy, we observed the spin-split states of single vacancy in graphite, which is a hallmark of magnetic states. Evolution of the spin splitting in the magnetic field did not follow the Zeeman effect of single electron states, and can be explained only when we consider electron-electron interaction. Quantitative analysis showed that the strength of the electron-electron interaction is in the range of 1~3 meV. Our observation implies that the simplest defect in graphite like single vacancy can behave as magnetic, which would be an important ingredient for development of carbon-based spintronic devices.

Scanning Probe Microscopy Focus Topic
Room Hall D - Session SP-TuP
Scanning Probe Microscopy Poster Session

SP-TuP1 New Directions in Ultrahigh Vacuum Tip-Enhanced Raman Spectroscopy with Molecular-Resolution Scanning Tunneling Microscopy, *Z. Porach, P. Whiteman,* University of Illinois at Chicago*; N. Chiang,* Northwestern University*; **Nan Jiang**,* University of Illinois at Chicago

During the last few years, the study of ultrahigh vacuum tip-enhanced Raman spectroscopy (UHV-TERS) has been raised to an unprecedented level. While scanning probe microscopy (SPM) is commonly used to study individual molecules, its information content can be severely compromised by surface diffusion, irregular packing, or three-dimensional adsorbate geometry. Here we demonstrate the simultaneous chemical and structural analysis of single molecules on the solid surface by UHV-TERS. In situ lenses can increase the collection efficiency with large numerical aperture. The strongly enhanced Raman signal makes the detection of single molecules possible. The adsorption configurations are able to be determined at unprecedented spatial resolution (<1nm).

SP-TuP3 Temperature-dependent Nanoscale Conductance on Water-Intercalated Graphene, ***JinHeui Hwang**, H. Lee, J.Y. Park,* Institute for Basic Science (IBS) & Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

We investigated the nanoscale conductace of water-intercalated graphene using current-sensing atomic force microscopy (C-AFM). The intercalation of water between graphene and mica was enabled by transfer of chemical vapor deposition (CVD) graphene on mica substrate. Water molecules were captured in the liquid water bath during the graphene transfer process. We show that the surface conductance are significantly influenced by the presence of water layer between graphene and mica. We found that the edge of water island exhibits the lower conductance, compared to that of bare graphene. We futher showed conductance of graphene on the first water layer were fluctuated depending on the temperature. The anomalous behavior of conductance is originated by structural defects of water layer and bonding nature between edge of the water islands and mica substrate, which lead to the suppression of the local current.

SP-TuP4 Phase Coexistence in Vanadium Dioxide Crystal Probed via Scanning Probe Microscopy, ***Christina McGahan**,* Vanderbilt University*; S. Gamage,* Georgia State University*; J. Liang,* Tianjin University, China*; B.G. Cross,* Georgia State University*; R.E. Marvel, R.F. Haglund,* Vanderbilt University*; Y. Abate,* Georgia State University

For the past decade, scattering-scanning near-field optical microscopy (s-SNOM) has been employed to image the coexisting metallic and insulating domains in single-crystal nanorods and platelets of vanadium dioxide (VO_2) during the insulator-to-metal phase transition. In virtually all studies, the coexisting domains appear as alternating stripes perpendicular to the c_R (growth axis) of the nanocrystals and extending from one side of the beam to the other.

We employed s-SNOM with a laser wavelength of **λ=**10.7 µm and polarized far-field optical microscopy to examine a single VO_2 microcrystal decorated with gold (Au) plasmonic dipole antennas. Metallic and insulating domains can be easily distinguished during the thermal phase transition in VO_2 using s-SNOM due to the large dielectric contrast between metallic and insulating VO_2 at that wavelength. Plasmonic dipole antennas are positioned on the crystal, designed to be resonant at the s-SNOM probe wavelength to allow simultaneous probing of the pattern of coexisting phases of VO_2 and the nanorod plasmon.

We observe a novel herringbone pattern of phase coexistence, seen in cracked epitaxial thin films but never in single crystals, in a VO_2 single crystal which is large enough that the phase coexistence is not constrained by high aspect-ratio geometry. The herringbone pattern is altered by the presence of ferroelastic strain domains that form to relieve stress and can nucleate metallic domains. These ferroelastic domains are imaged with polarized far-field optical microscopy. Though the local dielectric environment of the crystal changes during the phase transition, as indicated via s-SNOM, the plasmon resonance frequency of Au nanoantennas atop the crystal does not change in response to the growth of metallic domains. This indicates that the metallic domains nucleate in the bulk of the single crystal, beyond the range of the plasmon field, which only penetrates tens of nanometers below the crystal surface but in range of the s-SNOM due to the penetration depth of 10.7 µm laser light. The domain pattern is insensitive to the locations and orientations of the resonant Au antennas because the field, as determined through simulations, is not high enough to induce the VO_2 phase transition. Simulations indicate that a bowtie antenna has sufficient field to locally switch VO_2 from insulating to metallic, enabling localized induction of the phase transition near the surface of the VO_2.

SP-TuP5 Single Virus Particle Spectroscopic Nano-Imaging, ***Brendan Cross**, S. Gamage, M. Howard, J.R. Terrell, M. Luo, Y. Abate,* Georgia State University

We present the spectroscopic nano-imaging of single influenza virus particles in the mid infrared spectral region. The X-31 strain of Influenza A is an enveloped virus, which has a lipid and protein layer that contains the nucleocapsid. Virions are drop cast on silicon substrates for near-field imaging. High-resolution near-field microscopy is used to map the amide and phosphate bands of the envelope proteins on a single virion. We have also investigated the evolution of the virus as a function of time, acid treatment and laser radiation.

SP-TuP6 Spectroscopic Nano-Imaging Patterned InGaN Nanolayers, ***Alireza Fali**, S. Gamage, D. Seidlitz, I. Kankanamge, N. Dietz,* Georgia State University*; Y. Abate,* Georgia state university

Ternary InGaN compound semiconductors are of interest for many device applications such as light-emitting diodes, laser diodes, solar cells, etc., because they cover a broad spectral range from deep ultraviolet to near infrared as a function of the composition. This study focuses on nanoscopy of patterned structures of InGaN compound. To achieve this goal, InGaN film has been grown on top of the InN substrate. Scattering-type scanning near-field optical microscopy was used for nano-spectroscopic studies in the mid infrared spectral region of various thickness and composition of $In_{1-x}Ga_xN$ nanolayers grown on InN substrates.

SP-TuP7 Nanoscopy of Black Phosphorus Degradation, ***Sampath Gamage**,* Georgia State University*; L. Zhen,* University of Southern California*; V.E. Babicheva, M. Javani, V.S. Yakovlev,* Georgia State University*; H. Wang, S. Cronin,* University of Southern California*; Y. Abate,* Georgia State University

Black phosphorus (BP) is a promising layered material for optoelectronics applications due to its outstanding physical properties. Importantly, the thickness-dependent tunable direct bandgap of BP excited material scientists over graphene that lacks a natural bandgap. Similar to graphene, BP can be prepared commonly and simply by mechanical exfoliation. However, the major impediment of the BP based research is its surface degradation when exposed to atomospheric water and oxygen. In order to develop BP as a material for aforementioned applications, it is essential to understand degradation process at nanoscale chemical resolved resolution. In this poster contribution, we present our findings of the nanoscale spectroscopy degradation study of BP using scattering type scanning near-field optical microscopic (s-SNOM) technique at several mid infrared wavelengths. We have experimentally investigated the thickness dependence and substrate influence of a set of uncoated and Al_2O_3 coated samples and theoretically modeled the degradation evolution.

SP-TuP8 Periodically-pulsed Laser-Assisted Tunneling May Generate Terahertz Radiation, ***Mark Hagmann**,* University of Utah

Background: Periodic excitation of the tunneling junction in a scanning tunneling microscope by a mode-locked ultrafast laser superimposes a frequency comb at harmonics of the pulse repetition frequency on the DC tunneling current.[1] The power measured at the first 200 harmonics (74.254 MHz to 14.85 GHz) varies inversely with the square of the frequency—decaying only due to shunting by the stray capacitance.

Hypothesis: The tunneling junction is much smaller than the laser wavelength so effectively the laser superimposes a time-dependent voltage on the DC bias. Quasi-static conditions cause the time-dependent tunneling current to be related to the time-dependent voltage by a cubic polynomial as in the DC case. Thus, the waveform of the current in the tunneling junction is similar to the envelope of the laser radiation.

Analysis: The time-dependent voltage is modeled as a random process including pulse-jitter and finite coherence length of the laser. The current in the tunneling junction is shown to be a wide-sense stationary random process. For a laser with a pulse-width of 15 fs and pulse repetition frequency of 74.254 MHz the power spectral density in the tunneling junction has an intrinsic decay of 3 dB at the 2.4 x10^5th harmonic of 18 THz. The power measured at the first harmonic corresponds to a peak current of 5.7 nA. But the frequency of this harmonic is low enough that the decay caused by stray capacitance is negligible so this value, adjusted for the intrinsic decay, is the peak current at each harmonic in the tunneling junction.

Results and conclusions: Under the conditions for our measurements of the frequency comb we predict that in the tunneling junction the peak current for each pulse is approximately 690 mA. This value would be higher with a laser having greater coherence length or lower timing-jitter. It appears that the finest spatial resolution so far achieved in terahertz imaging is 40 nm by the near-field confinement of plane-wave illumination at a conical metal tip.[2] Our simulations suggest it may be possible to achieve atomic resolution by using the terahertz radiation at the tunneling junction in periodically-pulsed laser-assisted scanning tunneling microscopy. Much higher power is expected in periodically-pulsed laser-assisted field emission because of the greater current and much lower stray capacitance.

References

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Scanning Probe Microscopy Focus Topic
Room 104A - Session SP+SS+TF-WeM

Probing Electronic Properties

Moderator: Carl Ventrice, Jr., SUNY Polytechnic Institute

8:00am **SP+SS+TF-WeM1 Local Probe Investigation of 1D Structures and Interfaces in 2D Materials*, Chenggang Tao,*** Virginia Tech **INVITED**

Emerging two-dimensional (2D) materials, such as graphene and atomically thin transition metal dichalcogenides, have been the subject of intense research efforts for their fascinating properties and potential applications in future electronic and optical devices. The interfaces in these 2D materials, including domain boundaries and edges, strongly govern the electronic and magnetic behavior and can potentially host new quantum states. On the other hand, these interfaces are more susceptible to thermal fluctuation and external stimuli that drive mass displacement and generate disorder. In this talk we will present our scanning tunneling microscopy (STM) and spectroscopy (STS) explorations of edges of few layered molybdenum disulfide (MoS_2) nanostructures with unique structural and electronic properties and show how step edges on titanium diselenide ($TiSe_2$) surfaces change dynamically due to electrical fields. We will also discuss temperature evolution of quasi-1D C_{60} nanostructures on graphene. Through careful control of the subtle balance between the C_{60} surface mobility and the linear periodic potential of rippled graphene, C_{60} molecules can be arranged into a novel 1D C_{60} chain structure, and this chain structure can further transition to a compact hexagonal close packed stripe structure by tuning the annealing temperature.

8:40am **SP+SS+TF-WeM3 Investigation of Electronic Structures from Monolayers to Multilayers in Charge Transfer Complex, TTF-TCNQ using Low-temperature Scanning Tunneling Microscopy/Spectroscopy*, Seokmin Jeon*,** *P. Maksymovych,* Oak Ridge National Laboratory

The properties of few-layer molecular films are in general distinct from both bulk and monolayer phases, particularly in the case of metallic substrates, whose high-density electronic structure dominate the monolayer electronic structure and hamper characterization of the intrinsic properties of the molecular layer. This is especially true for charge transfer molecular solids, whose interesting electronic properties derive from a subtle alignment of each individual component's states, balance of dielectric screening, long-range electrostatic interactions, and relative molecular geometry. In contrast to vast effort on bulk phase study of the historic organic charge-transfer complex, TTF-TCNQ, study of its low-dimensional phases has been limited to monolayer phases. We investigated the evolution of the electronic structure of TCNQ and TTF-TCNQ multilayers using STM/STS at 4.3 K.

Thanks to submolecular resolution STM data and DFT calculations we were able to accurately determine the stacking relationship between the overlying layer and the underlying layer at an atomic scale. In such a well-defined layered model structure, we scrutinize the electronic structures of multilayered TCNQ and TTF-TCNQ using STS. Double-periodic charge ordering and Coulomb gap features are observed in the bilayer TTF-TCNQ. The effect of substrate variation (Ag, Au, and HOPG) on multilayer growth and electronic properties are discussed. The STS data from the multiple combinations of adsorbates and substrates allow us to assign states reliably and understand of transition of the surface, molecular, and charge transfer states clearly in the multilayer systems.

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

9:00am **SP+SS+TF-WeM4 Investigation of Initial Stages of Oxidation of Ni-Cr and Ni-Cr-Mo Alloys by Scanning Tunneling Microscropy/Spectroscopy (STM/STS)*, Gopalakrishnan Ramalingam*,** *P. Reinke,* University of Virginia

Ni-Cr based superalloys are excellent candidates for use in highly corrosive environments due to their exceptional oxidation and corrosion resistance. Our work focuses on unraveling the initial reaction steps of alloy oxidation as a function of composition, moving from the clean Ni-surface to a Ni-base alloy with 33wt% Cr. In the study presented here, we used STM/STS to investigate the initial stages of oxidation reaction in Ni-Cr (0-35wt.% Cr) alloys and the impact of Mo (2-10 wt.%) on the reaction. We developed spectroscopy maps which yield highly coveted information on the spatial distribution of oxide nuclei and the transition from chemisorbed oxygen to oxide. The STS maps capture the evolution of oxide during various stages of oxidation and provides valuable insight into the reaction as a function of composition of alloy.

Cr is the main alloying addition in Ni-based superalloys and the minimum amount of Cr necessary to form a continuous, passive oxide layer is 6-13 wt.% based on empirical observations. The passivating quality of an oxide layer strongly depends on the initial nucleation of the oxide, the oxide growth during continued oxidation, and eventual coalescence to form a complete oxide layer. However, the effect of Cr content on the initial nucleation and growth behavior of the oxide is not well understood. Similarly, the underlying mechanisms at the atomic scale and the role of electronic structure changes due to Mo addition are not well understood.

In this study, alloy thin films grown on MgO(100) substrates in an ultrahigh vacuum chamber are oxidized in situ at 300 °C with O_2 exposure up to 130 L. In the initial stages of oxidation (0.5-7 L of O_2), oxide nuclei are initially formed at the step-edges with some nucleation also present on the flat terraces. Subsequent oxygen exposure (>30 L) results in growth of existing oxide islands with additional nucleation of oxide. The amount of oxygen required for complete oxide coverage depends strongly on the Cr content of the alloy: >85% of the surface is covered with oxide in a Ni-14wt.%Cr alloy after 80 L oxidation while the same coverage is achieved in Ni-33wt.%Cr alloy after only 11.5 L. In contrast, we do not observe a complete oxide layer on Ni surface even after 180 L oxidation. Scanning tunneling spectroscopy maps provide spatially resolved electronic structure information and the variation of bandgap of the oxide as a function of oxide thickness and Cr content will be discussed. Preliminary data on the changes in the atomic and electronic structure of the thin film and oxidation behavior due to the addition of Mo will be presented.

9:20am **SP+SS+TF-WeM5 Au(111) Characterization, Single Atom Manipulation and Si(100):H Surface Imaging by LT-UHV-4 STM*, Corentin Durand*,** *D. Sordes, C. Joachim,* CNRS, France **INVITED**

Advance in nanotechnology requires the development of new instruments capable of imaging, communicating, manipulating and measuring at the atomic scale. The performances of the new ScientaOmicron LT-UHV 4-STM microscope have been certified by a series of state-of-art STM experiments on an Au(111) surface at 4.2 K [1]. During the STM operation of the 4 STM scanners (independently or in parallel), a Z stability of about 2 pm per STM was demonstrated. With this LT-UHV 4-STM stability, single Au atom manipulation experiments were performed on Au(111) by recording the pulling, sliding and pushing manipulation signals. Jump to contact experiments lead to perfectly linear low voltage I-V characteristics on a contacted single Au ad-atom with no need of averaging successive I-V's. Our results show that the 4 scanners of this new instrument working in parallel have performances equivalent to single tip state-of-art LT-UHV-STM. Two tips surface conductance measurements were performed on Au(111) using a lock-in technique in a floating sample mode of operation to capture the Au(111) surface states via two STM tips dI/dV characteristics. The capabilities of this microscope being demonstrated, we now move on to our next project, the realization of atomic devices. The hydrogen passivated Si(100) surface is a good candidate to achieve this goal. Here, I will show our preliminary results regarding the investigation of this surface and its topography. The surface has been prepared by a "wafer-bonding" method [2]. Large scale STM images show that this technique provides large and clean terraces essential to the fabrication of atomic circuits. Atomic resolution imaging enables us to confirm the position of the dimers, these latter ones having a different aspect depending on the polarity of the tunneling junction [3]. Finally, I will introduce the route of our project, the different steps we must achieve in order to build up a device made of few atoms on this surface [2].

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11:00am **SP+SS+TF-WeM10 Heterochiral to Homochiral Transition in Pentahelicene 2D Crystallization induced by 2nd-layer Nucleation*, Anaïs Mairena*,** Universität Zürich, Switzerland

Chirality is ubiquitous in our world (human body, pharmaceutics, liquid crystals…). Nevertheless, the principles of intermolecular recognition are still poorly understood. Therefore, it is not possible to predict the outcome of crystallization, which is still the most important method to separate chiral molecules into their enantiomers, or to explain why a minority of chiral compounds crystallize into conglomerate. A promising approach towards a better understanding of chiral interactions is the study of self-assembly of chiral molecules on single crystal surfaces with STM (sub-molecular resolution).

We studied the 2D self-assembly of racemic-pentahelicene ([5]H, $C_{22}H_{14}$) on Cu(111) with STM. Adsorption of [5]H leads, already at very low coverages to formation of homochiral pairs, i.e. both molecules have the same handedness.

At coverages close to the saturated monolayer, two distinct long-range ordered structures have been observed. Both structures have the homochiral pairs as building blocks. However, while one structure consists of a conglomerate of homochiral domains, the second structure is racemic, i.e. composed of homochiral pairs with opposite handedness. At monolayer coverage, only the racemic structure prevails. Above monolayer coverage, the dense racemate phase in the monolayer disappears on the expense of a homochiral conglomerate phase with lower density due to 2nd-layer-nucleation. Our results indicate that a long-range chiral communication between 2nd layer islands and other areas on the surface are at work.

These findings are also compared with those obtained for heptahelicene ($C_{30}H_{18}$) on Cu(111). A surface-mediated selection mechanism, taking different intermolecular interactions into account, will be presented.

11:20am **SP+SS+TF-WeM11 Two-stage Chiral Selectivity in the Molecular Self-Assembly of Tryptophan***, **Nathan Guisinger,*** Argonne National Laboratory*; B. Kiraly,* Northwestern University*; R. Rankin,* Villanova University

Both chirality and molecular assembly are essential and key components to life. In this study we explore the molecular assembly of the amino acid tryptophan (both L- and D- chiralities) on Cu(111). Our investigation utilizes low temperature scanning tunneling microscopy to observe resulting assemblies at the molecular scale. We find that depositing a racemic mixture of both L- and D- tryptophan results in the assembly of basic 6 molecule "Lego" structures that are enantiopure. These enantiopure "Legos" further assemble into 1-dimensional chains one block at a time. These resulting chains are also enantiopure with chiral selectivity occurring at two stages of assembly. Utilizing scanning tunneling spectroscopy we are able to probe the electronic structure of the chiral Legos that give insight into the root of the observed selectivity.

11:40am **SP+SS+TF-WeM12 Mask Free Approach to Selective Growth of Transition Metal Dichalcogenides Heterostructures enabled with Scanning Probe based Nanolithography***, R. Dong, L. Moore, N. Aripova, C. Williamson, R. Schurz,* Saint Louis University*; L.E. Ocola,* Argonne National Laboratory*; **Irma Kuljanishvili,*** Saint Louis University

Advances in graphene research ignited interest in other type of two-dimensional (2D) atomic crystals, such as hexagonal boron nitride and layered transition metal dichalcogenides (TMDCs). Among these new types of 2D materials, the applications of TMDCs in logic electronics and optoelectronics are promising because of their sizable bandgaps and natural stability. The techniques which enable heterostructure formation with different TMDCs systems have provided further solution to the design of high performance electronic devices such as those for photovoltaics and optoelectronics. The existing heterostructures fabrication methods, based on mechanical exfoliation and/or wet chemical transferring rely on traditional fabrication methods such as photo-and e-beam lithography.

To realize the selective growth and layered assembly of heterostructures at predefined location, here, we report on application of mask free, scanning probe based direct writing method. With the use of AFM cantilevers and developed water based "inks", we demonstrate arrays of MoS_2 and WS_2 dots and ribbon arrays at predefined locations on variety of substrates. Employing this SPM based patterning method we have also fabricated MoS_2/WS_2 heterostructures of sub-micrometer scales in a controlled fashion. The quality of MoS_2/WS_2 heterostructures was confirmed by Raman spectroscopy, AFM characterization and electrical transport measurements. Our mask free nanolithography approach offers an alternative route for patterning and growth of TMDCs with added benefit of potential reduced contamination of the TMDCs surfaces and interfaces between materials and substrates. It demonstrates a promising unconventional technology for fabrication of high quality TMDCs heterostructures in convenient manner capable of nanoscale precision.

Acknowledgements

Use of the Center for Nanoscale Materials was supported by the U. S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02 06CH11357. I.K. acknowledges support of NSF MRI program (Award No. 1338021), and the Saint Louis University seed funds.

12:00pm **SP+SS+TF-WeM13 Non-Destructive Electrical Depth Profiling across Nanometric SiO$_2$ Layers***, **Hagai Cohen,*** Weizmann Institute of Science, Israel*; A. Givon,* Tel Aviv University, Israel

The access to sub-nm scale depth information in thin dielectric layers, considering both the compositional and the electrical sub-surface characteristics, is challenging. A remarkable answer may be provided by CREM (chemically resolved electrical measurements), a technique based on x-ray photoelectron spectroscopy (XPS). CREM exploits the chemical contrast within a given structure to gain rich electrical information, or alternatively, apply electrical tests to gain improved structural&compositional analyses. Yet, for compositionally uniform domains, CREM becomes rather insensitive to the fine profiling details. Here, we show that this principal limitation can be overcome and the CREM resolution be improved significantly. Applied to nanometric silica layers, we reveal hidden impurity concentration profiles and further correlate them with the depth-dependent dielectric quality. Based on this leap improvement in resolution and sensitivity, our advanced CREM analysis promises diverse applications in device contact-free electrical studies.

Electronic Materials and Photonics
Room 102A - Session EM+NS+SP+SS-WeA

Nanoscale Imaging of Metals and Compound Semiconductor based Nanostructures, Surfaces and Interfaces

Moderators: Yohannes Abate, Georgia State University, Andy Antonelli, Nanometrics

2:20pm **EM+NS+SP+SS-WeA1 The Importance of Contact Engineering for 2D Devices***, **Saptarshi Das,*** Pennsylvania State University **INVITED**

Contact resistance is one of the most important factors which could potentially limit the performance of novel electronic and optoelectronic devices based on two-dimensional (2D) materials like graphene, black phosphorus, various transition metal dichalcogenides (TMDs) like MoS_2, WSe_2 and beyond [1-3]. It is now widely accepted that metal-2D contacts are mostly Schottky barriers type [1-3]. Hence, various contact engineering strategies have been adopted to minimize the Schottky barrier height at the metal-2D interface and thereby reduce the contact resistance. In this talk I will provide a comprehensive overview of different contact engineering schemes metal work function engineering, interface engineering and phase engineering [4-6]. Additionally, I will also talk about the scalability of the contact resistance since an aggressively scaled 2D device will also have aggressively scaled contacts.

1. Das S, Chen H-Y, Penumatcha AV, Appenzeller J: **High performance multilayer MoS2 transistors with scandium contacts**. *Nano letters* 2012, **13**(1):100-105

2. Das S, Appenzeller J: **WSe2 field effect transistors with enhanced ambipolar characteristics**. *Applied Physics Letters* 2013, **103**(10):103501

3. Das S, Demarteau M, Roelofs A: **Ambipolar phosphorene field effect transistor**. *ACS nano* 2014, **8**(11):11730-11738.

4. Das S, Appenzeller J: **Where does the current flow in two-dimensional layered systems?***Nano letters* 2013, **13**(7):3396-3402

5. Das S, Gulotty R, Sumant AV, Roelofs A: **All two-dimensional, flexible, transparent, and thinnest thin film transistor**. *Nano letters* 2014, **14**(5):2861-2866.

6. Kappera R, Voiry D, Yalcin SE, Branch B, Gupta G, Mohite AD, Chhowalla M: **Phase-engineered low-resistance contacts for ultrathin MoS2 transistors**. *Nature materials* 2014, **13**(12):1128-1134.

3:00pm **EM+NS+SP+SS-WeA3 Imaging Stress-Directed Compositional Patterning in Silicon Germanium with μ-Raman Spectroscopy***, **Brian Rummel**, S.M. 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 an epitaxial compound semiconductor film.[1] This compositional patterning laterally manipulates quantum barriers within the film in a press-and-print manner. In this example, an array of silicon pillars is pressed against a relaxed $Si_{0.8}Ge_{0.2}$ substrate in a mechanical press, and the entire assembly is heated to high temperatures. This serves to promote a diffusive separation of the germanium into highly localized regions. Here, the difficulty in analyzing these structures is due to the lack of surface detail on the stress-annealed substrate as there is only elastic deformation observed during the fabrication process. To visualize the regions compressively stressed by the pillars and therefore compositionally altered regions, we report the use of μ-Raman spectroscopy to produce a 2D compositional map of a substrate. The substrate is patterned with feature sizes on the order of 1 to 3 microns to remain within the spatial resolution of μ-Raman spectroscopy for the purpose of demonstration. The first-order Raman spectrum for pure silicon and germanium produces peaks at 520.2 and 300.7 cm^{-1}, respectively. The deviations from these relaxed silicon and germanium peaks have been attributed to residual tensile stress in the Ge-depleted regions. Lateral line scans are performed to map the compositions of the stressed and annealed substrate, which provides a clear image of the resulting diffusion process. This imaging also allows the quantum structures to be addressable.

[1] S. Ghosh, D. Kaiser, J. Bonilla, T. Sinno, and S. M. Han, "Stress-Directed Compositional Patterning of SiGe Substrates for Lateral Quantum Barrier Manipulation," *Applied Physic Letters* **107,** 072106-1:5 (2015).

3:20pm **EM+NS+SP+SS-WeA4 Atomic-scale Characterization of III-V Nanowire Heterostructures and Devices***, J. Knutsson, S. McKibbin, M. Hjort, J. Colvin, S. Yngman, A. Troian, O. Persson, A. Mikkelsen, **Rainer Timm**,* Lund University, Sweden

III-V semiconductor nanowires (NWs) have a large technological potential within electronics, optoelectronics, and energy harvesting [1]. With their flexibility in creating heterostructures, by radial and axial stacking during epitaxial growth, comes an increasing complexity of device structure. Furthermore, due to their small diameter and their very large surface-to-volume-ratio, the performance of NW devices is strongly determined by surface properties. It is therefore essential to study the structural and electronic properties of NW surfaces down to the atomic level and across interfaces regarding doping, material composition, or crystal phase.

We recently obtained atomically resolved scanning tunneling microscopy (STM) images of various GaAs, InAs, and InP NW surfaces [2,3]. By combining STM imaging with scanning tunneling spectroscopy (STS) measurements, we correlate the surface structure and local electronic properties [3]. Here, we will present examples from InAs NWs with interfaces between different crystal phase. Our low-temperature STM/S results show that even the smallest possible insertion of zincblende phase within a wurtzite segment, a single bilayer stacking fault, shows a clear zincblende signature. We observe transitions in the local density of states with sub-nm lateral resolution. Furthermore, we map the interface band alignment and measure quantum confinement energies of single and double bilayer stacking faults.

Beyond traditional steady-state surface characterization, it is desirable to even investigate nanostructure devices *in-situ*, meaning while they are operating under an applied bias. We are now using simultaneous STM, AFM, and electrical transport measurements for studying individually contacted NWs during device operation [4], complemented by Kelvin probe force microscopy and scanning photoemission microscopy. We will present initial results of such combined *in-situ* studies on axial *pn*-junctions in InP and GaInP NWs, where we also investigate the influence of NW surface modification (e.g. removal of native oxide by atomic hydrogen) on photovoltaic properties.

[1] E. Lind *et al.,* IEEE J. El. Dev. Soc. **3**, 96 (2015); J. Wallentin *et al*., Science **339**, 1057 (2013).

[2] M. Hjort *et al*., ACS Nano **6**, 9679 (2012); J. Knutsson *et al.,* ACS Appl. Mat. & Interf. **7**, 5748 (2015).

[3] M. Hjort *et al*., Nano Lett. **13**, 4492 (2013); M. Hjort *et al.,* ACS Nano **8**, 12346 (2014).

[4] O. Persson *et al.,* Nano Lett. **15**, 3684 (2015); J. L. Webb *et al*., Nano Res. **7**, 877 (2014).

4:20pm **EM+NS+SP+SS-WeA7 Revealing Optical Properties of Reduced-Dimensionality Materials at Relevant Length Scales using Nanospectroscopic Imaging***, **P. James Schuck**,* The Molecular Foundry, Berkeley Lab **INVITED**

Reduced-dimensionality materials for photonic and optoelectronic applications including energy conversion, solid-state lighting, sensing, and information technology are undergoing rapid development. The search for novel materials based on reduced-dimensionality is driven by new physics. Understanding and optimizing material properties requires characterization at the relevant length scale, which is often below the diffraction limit. The nano-optical imaging community has now crossed the boundary from insufficient to sufficient resolution, mapping critical optoelectronic properties in these exciting materials at their native length scales. Here, I will describe the recent near-field imaging advances that lay groundwork for generally-applicable nano-optical studies of these low-D materials, and will show recent results on 0, 1, and 2D systems. I will spend time discussing the importance of near-field polarization in probing these materials, and will also highlight recent applications in 2-D semiconductor transition metal dichalcogenides (TMDCs), where we and others have uncovered new optoelectronic regions and spatially-varying features that were hidden in prior optical studies. These findings have broad implications for the development of atomically thin transistors, quantum optical components, photodetectors and light-emitting devices.

5:00pm **EM+NS+SP+SS-WeA9 Polarizability Mapping of Nanolayers Based on Near-Field Edge Fringes***, **Viktoriia Babicheva**, V.S. Yakovlev, S. Gamage, M.I. Stockman, Y. Abate,* Georgia State University

Scattering-type scanning near-field optical (s-SNOM) microscopy enable spectroscopic imaging with nanoscale resolution and provide chemical and structural information of surfaces [1]. In this work, we investigate identification of material type using an approach based on analyzing near fields at the sample edge [2]. We develop theoretical approach that includes full-wave numerical simulations and calculations of s-SNOM signal in different demodulation orders. This model allow characterization of structures of any shape and material, as well as different tips, and does not include any fitting parameters. In this way, we defined that metallic edge has bright and dark fringes in near-field characterization, whereas a bright edge of dielectric material has no outside fringe. Similar behavior is observed for anisotropic material with hyperbolic dispersion (boron nitride in mid-IR range): depending on the wavelength, it shows either metallic or dielectric properties.

1. Y. Abate, R.E. Marvel, J.I. Ziegler, S. Gamage, M.H. Javani, M.I. Stockman, and R.F. Haglund "Control of plasmonic nanoantennas by reversible metal-insulator transition" Sci. Rep. 5, 13997 (2015).

2. Y. Abate, S. Gamage, L. Zhen, S.B. Cronin, H. Wang, V. Babicheva, M.H. Javani, M.I. Stockman, "Nanoscopy reveals metallic black phosphorus," Light: Science & Applications, accepted (2016). http://arxiv.org/abs/1506.05431

5:20pm **EM+NS+SP+SS-WeA10 Wedding Cake Growth Mechanism in One-Dimensional and Two-Dimensional Nanostructure Evolution***, **Xin Yin**[*],* University of Wisconsin-Madison*; J. Shi,* Rensselaer Polytechnic Institute*; X. Niu,* Northeastern University*; D. Geng,* University of Wisconsin-Madison*; H. Huang,* Northeastern University*; X.D. Wang,* University of Wisconsin-Madison

Morphology is one essential element that gives rise to extraordinary physical, chemical, and mechanical properties in nanomaterials. Precise morphology control of nanomaterials is a notorious task, which heavily relies on fundamental understanding of the governing atomistic mechanisms and kinetics at the nanoscale. Despite numerous studies on the growth and application of nanostructures, current understanding of kinetics that governs the nanocrystal evolution is yet limited.

By programming deposition conditions at time domain, we observed the wedding cake growth mechanism in the formation of 2D ZnO nanostructures. Within a narrow growth window, the surfaces of 2D structures were covered with a unique concentric terrace feature. This mechanism was further validated by comparing the characteristic growth rates to the screw dislocation-driven model. An interesting 1D to 2D morphology transition was also found during the wedding cake growth, when the adatoms overcome the Ehrlich-Schwoebel (ES) barrier along the edge of the top crystal facet triggered by lowering the supersaturation. The evolution of 2D plate structure from 1D pillars represents a dynamic crystal growth behavior transition when the local deposition conditions were tuned in-situ. It lively recorded the wedding cake growth model in nanostructure formation from vapor phase, which was rare to be observed when the deposition conditions were remained constant. The terrace feature on these nanostructures provided a valuable platform for understanding the wedding cake growth kinetics that could be an important mechanism to design and predict the nanocrystal morphology formation from the bottom-up. Analyzing the supersaturation and temperature-related growth behavior provides a new insight into nanostructure growth mechanisms and morphology control.

Wedding cake growth is a layer-by-layer growth model commonly observed in epitaxial growth of metal films, featured by repeated nucleation of new atomic layers on the topmost surface owing to the confinement of the Ehrlich–Schwoebel (ES) barrier. This study expands the application of the wedding cake growth mechanism to the nanostructure growth. It enriches our understanding on the fundamental kinetics of nanostructured crystal growth and provides a transformative strategy to achieve rational design and control of nanoscale geometry.

5:40pm **EM+NS+SP+SS-WeA11 Detecting the Invisible - The Atomic Structure of Radiation Sensitive Nano-Materials***, **Christian Kisielowski**,* Molecular Foundry, Lawrence Berkeley National Laboratory*; P. Specht,* University of California Berkeley **INVITED**

As heterogeneous materials scale below 10 nm, a suitable combination of single digit nanocrystals with their rich variety of tunable surfaces and interfaces allows tailoring unprecedented materials with novel structure-function relationships. The design of new catalysts [1], investigations of polymers at atomic resolution [2] or analyses of deviations from a random doping distributions at atomic resolution [3] may serve as examples. This contribution describes research that aims at exploiting the emerging ability to analyze and understand such materials by directly determining their atom arrangement in three-dimensions using aberration-corrected transmission electron microscopy [4]. Attempts to unravel the atomic structure of such nanoscale composites in this manner must explicitly address their pronounced sensitivity to the probing radiation that can unintentionally alter their pristine structure, often beyond recognition. We address this challenge by applying low dose-rate in-line holography [5], which allows operating electron microscopes with dose rates as low as 5-10 e/Å^{2}s that help maintaining structural integrity at atomic resolution to an unexplored end. The approach mimics best practices in biological research but achieves atomic resolution with single atom sensitivity by the acquisition of large image series. We observe a variety of previously unknown atom configurations in surface proximity of CoO_x nanocrystals and coatings that are hidden behind unusually broadened diffraction patterns but become visible in real space images because the phase problem is solved. The observed structures are drastically altered by an exposure of the material to water vapor or other gases, which is investigated at atomic resolution in environmental electron microscopy. It is shown for Rh/W catalysts that electron beam-induced atom dynamics can be entirely suppressed even for atom clusters made from less than 10 atoms. Resultantly, chemical compositions can be determined by contrast measurements alone and functional processes can be triggered and tracked in real time at atomic resolution.[6]

[1] J. A. Haber et al., **Advanced Energy Materials** 5 (2015) 1402307

[2] D. Lolla et al., **Nanoscale** 8 (2016) 120 - 128

[3] P. Specht, C. Kisielowski, On the chemical homogeneity of InxGa1-xN alloys - Electron microscopy at the edge of technical limits, submitted (2016)

[4] F.R. Chen et al., **Nature Commun**. 7:10603 doi: 10.1038/ ncomms10603 (2016)

[5] C. Kisielowski, **Advanced Materials** 27 (2015) 5838-5844

[6] The Molecular Foundry, which is supported by the Office of Science, the Office of Basic Energy Sciences, the U.S. Department of Energy under Contract No. DE-AC02-05CH11231

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[*] **NSTD Student Award Finalist**

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