

2D Materials Technical Group

Room 303 - Session 2D+AS+NS+SS-ThM

2D Materials: Scanning Probe Microscopy and Spectroscopy

Moderators: Matthias Batzill, University of South Florida, Yi-Ting Hsu, University of Notre Dame

8:00am **2D+AS+NS+SS-ThM-1 Atomically Precise Graphene Nanoribbons for Quantum Electronics**, *An-Ping Li*, Oak Ridge National Laboratory

INVITED

An-Ping Li, Chuanxu Ma, Marek Kolmer, Wonhee Ko, Kunlun Hong, Peter Bonnesen, Alex Puzetzy, Jingsong Huang, Liangbo Liang, Bobby Sumpter

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Graphene nanoribbons (GNRs) possess high mobility and current-carrying capability, sizeable bandgap, long mean free path, localized spin and topological edge states [1]. These properties make them attractive candidates for quantum electronic applications. Atomically precise GNRs can be synthesized bottom-up using controlled on-surface chemical reactions from rationally designed molecular precursors [2]. The on-surface reactions of molecular precursors performed under ultra-high vacuum conditions can further be combined with scanning tunneling microscopy (STM) for in situ characterization of atomic, electronic, and magnetic properties. In this talk, I will discuss our recent progress in realizing novel quantum states in GNR heterostructures at atomic precision. First, a bottom-up approach is developed to couple graphene nanodot (GND) covalently at the edges of GNR to create quantum-well-like states for well-defined narrow-band light emission [3], which highlights a route to programmable and deterministic creation of quantum light emitters. Second, atomically precise GNRs are obtained by the on-surface synthesis approach on a model metal oxide, showing entangled magnetic states decoupled from the substrate [4]. These works illustrate that by using bottom-up synthesis—complemented by advanced microscopy and spectroscopy, as well as theory/simulation to enable atomistic level control—a rational approach to graphitic quantum electronic materials can be established with atomic precision.

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[1] H. Wang et al., Graphene nanoribbons for quantum electronics, *Nat. Rev. Phys.* 3, 791 (2021). <https://doi.org/10.1038/s42254-021-00370-x>

[2] C. Ma et al., On-surface cyclodehydrogenation Reaction Pathway Determined by Selective Molecular Deuterations, *Chemical Science* 12, 15637 (2021). <https://doi.org/10.1039/D1SC04908A>

[3] C. Ma et al., Engineering Edge States of Graphene Nanoribbons for Narrow-Band Photoluminescence, *ACS Nano* 14, 5090 (2020). <https://doi.org/10.1021/acsnano.0c01737>

[4] M. Kolmer et al., Rational synthesis of atomically precise graphene nanoribbons directly on metal oxide surfaces, *Science* 369, 571 (2021). <https://www.science.org/doi/10.1126/science.abb8880>

8:40am **2D+AS+NS+SS-ThM-3 Band Gaps of Single-Layer Transition-Metal-Dichalcogenides Determined by Scanning Tunneling Spectroscopy**, *Randall Feenstra*, G. Frazier, J. Lou, Carnegie Mellon University; Y. Pan, S. Foelsch, Paul Drude Institute, Germany; Y. Lin, B. Jariwala, K. Zhang, J. Robinson, Penn State University

Using scanning tunneling spectroscopy at a temperature of 5 K, the electronic states of single-layer MoS₂ and WSe₂, grown on epitaxial graphene, have been investigated. Data is acquired utilizing a high-dynamic-range method in which the sample-tip separation is varied as a function of the sample-tip voltage (separation is decreased linearly as the magnitude of the voltage is reduced). Resulting spectra, when normalized to constant sample-tip separation, display conductance values that range over 5 – 6 orders of magnitude above the noise level [1]. The resulting edges of the conduction and valence bands, as well as onsets of higher/lower lying bands, are clearly defined. A theory for fitting the spectra is developed in which the varying wave-vector of the electronic states is explicitly included, yielding significant improvement in the quality of the fits compared to prior work [2]. Band onset energies can be determined with an accuracy of ~20 meV [1]. However, certain features in the data remain poorly explained by the model, in particular, an apparent broadening or smearing of the band edges which is 5x larger than that

given by any instrumental effect (kT broadening together with modulation voltage of the measurement). Tentatively, this additional broadening is attributed to tip-induced band bending. Results of fitting which includes this effect will be described.

[1] R. M. Feenstra, G. R. Frazier, Yi Pan, St. Fölsch, Y.-C. Lin, B. Jariwala, K. Zhang, and J. A. Robinson, *J. Vac. Sci. Technol. A* 39, 011001 (2021). P. Mårtensson and R. M. Feenstra, *Phys. Rev. B* 39, 7744 (1989).

[2] H. M. Hill, A. F. Rigosi, K. T. Rim, G. W. Flynn, and T. F. Heinz, *Nano Lett.* 16, 4831 (2016).

9:00am **2D+AS+NS+SS-ThM-4 Open-Source Controller for Scanning Probe Microscopy Applications**, *M. Kanqül, N. Asmari Saadabad, M. Penedo, Georg Fantner*, École Polytechnique Fédéral de Lausanne, Switzerland

Transferring the outcomes of academic research into patented industrial products converts the conceptual proof into accessible and sustainable technology. However, it is not always beneficial for researchers; as scientific studies often push the limits of instruments, requiring custom functionalities. In order to resolve these needs, several options are available, among which, hacking off-the-shelf products or rebuilding a simple copy of the existing technology are the most common ones. Either of these solutions slows down the research in a multidisciplinary field like Scanning Probing Microscopy (SPM). To not be limited by the disadvantages of the aforementioned solutions, we have developed an open-source SPM controller as a technology that eases innovation in not only our research but also in the whole SPM community.

In this regard, we have chosen a modular design strategy. A commercial FPGA (NI-7856R) with embedded real-time controller code sits at the core of the controller hardware. An FPGA adapter board for the flexibility of choosing different FPGAs, interconnect boards to perform digitally controlled (SPI) analog signal conditioning, such as filters and gain-offset stages, and a microscope adapter board to easily customize the input/output terminals of the controller for various SPM instruments are the other components of the modular hardware design. To run the controller, a custom software suite was developed in the graphical programming language LabVIEW (National Instruments). Similar to hardware, the software is also implemented in a highly modular fashion. The functions have been formulated into separate modules with minimum cross-dependency to reduce the complexity of coding for new developers.

The interest of our scientific and industrial collaborators in adapting and using our SPM controller in their instruments has motivated us to put an extra effort into building supporting documentation and creating an open-source platform. For the hardware, the documentation comprises design files, manufacturing guides, and assembly notes. For the software, documentation explaining the functionality of the real-time controller is provided, while the user interface side of the software is documented with user guides.

Here we report an open-source modular SPM controller provided with detailed documentation on both hardware and software levels. Modularity and documentation make it an easy-to-adapt instrument for various SPM applications. This platform has already been successfully adapted to control different SPMs such as contact mode AFM, AM-AFM, high-speed off-resonance tapping mode AFM, scanning ion conductance microscope, correlative AFM/SEM, and STM.

9:20am **2D+AS+NS+SS-ThM-5 Activation of Resistive Switching in TaOx on the Nanoscale**, *Olha Popova*, ORNL

In present work we have shown two alternative pathways to induce resistive switching of prototypical TaOx –(1) via direct biasing with a nanoscale AFM probe in oxygen free environment and (2) via He-ion patterning. Both approaches were carried out with fine control over the net amount of dissipated energy during activation. With direct AFM probe activation in oxygen free environment, we were able to switch conducting properties of the material in poorly controlled conditions. This is a similar pathway to electroforming, albeit combined with microscopy, which revealed directly the changes induced in the film during field-induced insulator-metal transition. Filamentary regions down to 20 nm in dimension could be routinely achieved by reducing the peak current during the activation cycle. Nevertheless, the process remains extremely stochastic. In contrast, by use of He ion irradiation pristine insulating state can be easily converted to conducting and resistively switching state without any breakdown, but the transition itself is a smooth function of

Thursday Morning, November 10, 2022

ion-irradiation dose. These findings revealed numerous intermediate states of TaOx can be created by controlled ion-irradiation. Remarkably, this effect is directly compatible with device architectures, potentially allowing for a high-degree of on-demand tuning of neuromorphic circuitry and materials. By combining AFM and SEM-CL we were able to determine dependence of the ion dose/materials damage correlated with the chemical, structural and compositional tunability of thin TaOx films which offers significant opportunities to neuromorphic nanoelectronic materials in comparison with more mature technologies based on traditional bulk electronic materials.

9:40am **2D+AS+NS+SS-ThM-6 Probing Sub-Nanoscale Photophysical and Photochemical Processes via Localized Surface Plasmons: Vibrational Nano-Spectroscopy**, *Sayantan Mahapatra, N. Jiang*, University of Illinois - Chicago

Conventional spectroscopic techniques are limited by the optical diffraction limit to about half wavelength and therefore offer about 200 nm x 200 nm microscopic zone for working in the visible light range. Tip-enhanced Raman spectroscopy (TERS) emerges as an advanced analytical technique, where the plasmonically active probe is not only used to detect the tunneling current but also to interrogate the local chemical environment of the surface adsorbed molecules with angstrom scale precision. In this work, we report a topological and chemical analysis of two regioisomers (positional isomers), trans- and cis-tetrakis(pentafluorophenyl)porphodilactone (trans- and cis-H₂F₂₀TPPDL) by scanning tunneling microscopy (STM), ultrahigh vacuum (UHV) TERS on Ag(100) with the spatial resolution down to 8 Å, which has a wide range of applications in various field of surface science & nanotechnology such as regioselective catalysis reaction, chemical reactions, molecular electronics, etc. We have shown that it is possible to distinguish these two structurally very similar forms with high accuracy & precision. The two-component molecular junction has been identified using high resolution two-dimensional (2D) Raman mapping. Furthermore, the nanoscale molecule-substrate interactions have been addressed at the single-molecule level by employing different single-crystals i.e., Ag(100), Cu(100), and Au(100). Strong surface interactions at Cu(100) surface converted the flexible porphodilactone structure inverted, which was further verified by STM. In another case, the chemical transformation of adsorbed ferrocene dicarboxylic acid molecule was also analyzed via TERS on Cu(100) due to significantly strong interaction. Apart from the Raman signal enhancement, the highly energetic localized surface plasmons generated at the tip apex were utilized for site-selective C—Si bond activation inside a single 5,10,15,20-(tetra-trimethylsilylethynyl)porphyrin molecule. The nano-confined plasmonic field dissociated only one chemical bond, in presence of multiple chemically equivalent bonds inside the single molecule. To this end, multiple sites were also activated one by one and different types of products were visualized which could prove extremely useful in plasmon-induced site-selective heterogeneous catalysis application.

11:00am **2D+AS+NS+SS-ThM-10 Visualize Emergent Electron Orders in Two-Dimensional Quantum Materials**, *Xiaomeng Liu*, Princeton University
INVITED

Recent developments have enabled scientists to isolate various 2D materials and assemble them into van der Waals heterostructures with elaborate stacking and alignments. These van der Waals materials, constructed layer-by-layer, host numerous novel quantum phases. However, most studies so far are done by electrical transport measurements, lacking spatial and energy resolution. Scanning tunneling microscopes (STM) can provide unique insights to these emergent quantum phases by visualizing the electron wave function in real space. Using our recent study of the graphene quantum Hall system as an example, I will demonstrate using STM techniques to identify broken symmetries, visualize electron wavefunctions, and imaging quasiparticles.

11:40am **2D+AS+NS+SS-ThM-12 Reconstruct the Intrinsic Force Landscape of Interfacial Interaction with Excitation-Enhanced Force Spectroscopy**, *Alan Liu, T. Sulchek*, Georgia Institute of Technology

The advancement of sensitive force transducers has enabled scientists to measure the subtle forces of interactions between molecules and interfaces at nanometer scales. Force spectroscopy techniques, such as dynamic force spectroscopy (DFS), extract a single representative force from each measurement, and require thousands of measurements with model assumptions to extract useful physical parameters of the interaction. This process is not only time consuming, but also the preciseness of the results relies largely on model assumptions, which make

the results highly variable and dependent on experimental conditions. Furthermore, because DFS models presume the interaction to be a reversible reaction under certain energy/force landscape, parameters extracted by DFS method can only represent the rough shape of interaction landscape but not able to probe the detail landscape of underlying intrinsic interactions. Using our recently developed force spectroscopy framework¹, we can obtain the definitive intrinsic force landscape using a high sampling rate (above 1 MHz) atomic force microscopy (AFM) measurement. While most studies deemed the “snap” of AFM force measurement as an instantaneous action, we successfully sampled the fluctuation and real-time movement of the AFM probe at snap under a high sampling rate. At the snap location of each AFM force-distance measurement, transition points can be identified that define the bound state (or probe-in-contact state) and unbound state (or free oscillation state). Sampling at these transition points are key to probe the normally inaccessible portion of force landscape where the intrinsic force landscape has higher force gradient than the stiffness of the force probe. Next, we demonstrated how to modulate the snap locations of the force-distance curves by tuning the bandwidth of the excitation applied to the AFM probe. Lastly, we integrated the definitive forces sampled at various locations to reconstruct the intrinsic force landscape of the interaction without any model assumption or curve fitting process.

[1] Alan Y. Liu and Todd A. Sulchek, Reconstructing the Intrinsic Potential Energy Landscape of Interfacial Interactions with Thermally Modulated Force Spectroscopy, *Phys. Rev. Res.* 3, (2021).

12:00pm **2D+AS+NS+SS-ThM-13 AVS Graduate Research Awardee Talk: True Atomic-Resolution Imaging under Ambient Conditions via Conductive Atomic Force Microscopy**, *Saima Sumaiya¹, M. Baykara*, University of California, Merced

Atomic-scale characteristics of surfaces dictate not only the governing principles of numerous scientific phenomena ranging from catalysis to friction, but also the design and performance of billions of state-of-the-art nanoscale devices ubiquitous in modern life. Despite such an enormous significance, our ability to visualize surfaces on the atomic scale is severely limited by the strict conditions under which the related methods are operated. In particular, the two prominent methods utilized to achieve atomic-resolution imaging – scanning tunneling microscopy (STM) and noncontact atomic force microscopy (NC-AFM) – are typically performed under ultrahigh vacuum (UHV) and often at low temperatures. Perhaps more importantly, results obtained under such well-controlled, clean environments bear little relevance for the great majority of processes and applications that often occur under ambient conditions. Therefore, a method which is able to reliably and robustly image surfaces with atomic-level spatial resolution under ambient conditions can be regarded as a “holy grail” of surface science. Here, we first show that the method of conductive atomic force microscopy (C-AFM) can be utilized to achieve true atomic-resolution imaging under ambient conditions by imaging single atomic vacancies on molybdenum disulfide (MoS₂), without any control over the operational environment or elaborate sample preparation. With our method, we are also able to image several other types of defects on MoS₂, demonstrating that C-AFM can be utilized to investigate surface defects in a reliable, straightforward fashion under ambient conditions, in contrast to the often extensive operational requirements of STM and NC-AFM. We further employ the method of C-AFM to record atomic-resolution images on different classes of materials such as gold (metal), WSe₂ (semiconductor), PtSe₂ (semimetal), and α-Mo₂C (metallic transition metal carbide), proving its versatility in terms of the material classes it can be applied to. Our approach overcomes many of the classical limitations associated with STM and NC-AFM, and the findings herald the emergence of C-AFM as a powerful tool for atomic-resolution imaging under ambient conditions.

¹ AVS Graduate Research Awardee

Author Index

Bold page numbers indicate presenter

— A —

Asmari Saadabad, N.: 2D+AS+NS+SS-ThM-4,
1

— B —

Baykara, M.: 2D+AS+NS+SS-ThM-13, 2

— F —

Fantner, G.: 2D+AS+NS+SS-ThM-4, **1**

Feenstra, R.: 2D+AS+NS+SS-ThM-3, **1**

Foelsch, S.: 2D+AS+NS+SS-ThM-3, 1

Frazier, G.: 2D+AS+NS+SS-ThM-3, 1

— J —

Jariwala, B.: 2D+AS+NS+SS-ThM-3, 1

Jiang, N.: 2D+AS+NS+SS-ThM-6, 2

— K —

Kangül, M.: 2D+AS+NS+SS-ThM-4, 1

— L —

Li, A.: 2D+AS+NS+SS-ThM-1, **1**

Lin, Y.: 2D+AS+NS+SS-ThM-3, 1

Liu, A.: 2D+AS+NS+SS-ThM-12, **2**

Liu, X.: 2D+AS+NS+SS-ThM-10, **2**

Lou, J.: 2D+AS+NS+SS-ThM-3, 1

— M —

Mahapatra, S.: 2D+AS+NS+SS-ThM-6, **2**

— P —

Pan, Y.: 2D+AS+NS+SS-ThM-3, 1

Penedo, M.: 2D+AS+NS+SS-ThM-4, 1

Popova, O.: 2D+AS+NS+SS-ThM-5, **1**

— R —

Robinson, J.: 2D+AS+NS+SS-ThM-3, 1

— S —

Sulchek, T.: 2D+AS+NS+SS-ThM-12, 2

Sumaiya, S.: 2D+AS+NS+SS-ThM-13, **2**

— Z —

Zhang, K.: 2D+AS+NS+SS-ThM-3, 1