

## Nanoscale Science and Technology Division Room On Demand - Session NS-Contributed On Demand

### Nanoscale Science and Technology Contributed On Demand Session

#### NS-Contributed On Demand-1 Precision Control of Cavity Quantum Electrodynamics in Space-Time with fsTHz-STM, *Likun Wang, Y. Xia, W. Ho*, University of California Irvine

Cavity quantum electrodynamics (QED) for a molecular two-level system interacting with quantized terahertz photons has been realized by combining a femtosecond THz laser with a low temperature scanning tunneling microscope (fsTHz-STM). A hydrogen molecule adsorbed in a Cu<sub>2</sub>N island grown on the Cu(100) surface and under the STM tip develops a dipole moment, becoming a two-level system in a double-well potential. A Stark effect is measured from the electric field by changing the junction bias. Time domain measurements by varying the delay of the pump-probe THz pulses reveal the coherent superposition of the two-level states. By decreasing the tunneling gap, the strong coupling regime is reached, leading to cavity-QED of the superposition of a single photon with the two-level states of a single hydrogen molecule within the STM junction cavity of sub-nm dimensions. An avoided crossing is observed as a function of the junction electric field in the transition from the ground state to the doublet superposition states. The photon-molecule coupling strength is directly obtained from the energy gap at the minimum of the avoided crossing. By tuning the tunneling gap and tip position with sub-Ångström precision, the coupling strength has been increased from zero to 25% of the energy separation of the two-level states. These results demonstrate electric control of the THz induced transitions to the superposition of photon-molecule cavity-QED states, enabled by measurements with simultaneous spatial and temporal resolutions, and suggest the use of molecules as qubits and carriers of quantum information.

#### NS-Contributed On Demand-4 RF Plasma for the Facile Fabrication of Bio-Functional Polymeric Nanoparticles, *Laura Haidar*, University of Sydney, Australia

Multifunctional polymeric nanoparticles have advanced the field of nanotechnology, particularly biomedicine, by introducing a promising platform for targeted delivery, diagnostics, and therapeutics. Their surfaces can be conjugated with ligands such as proteins, peptides, pDNAs, fluorescent markers and drugs for versatile applications ranging from site-specific targeting, to bioactive delivery, cancer therapy, bioimaging and topical immunization. Conventionally, the functionalization of polymeric nanoparticles incorporates tedious wet-chemical processes that require multi-step protocols with high-cost disadvantages. Plasma polymerized nanoparticles (PPNs) produced through a simple, dry low-pressure plasma process can attain tunable radical-rich platforms that enable the direct attachment of ligands. In this study, we explored a C<sub>2</sub>H<sub>2</sub>/N<sub>2</sub>/Ar plasma as a rapid and cost-effective source to fabricate highly reactive particles capable of being functionalized with bio-active molecules. The discharge was generated by capacitively coupling the rf power ( $f = 13.56$  MHz) to the plasma and is characterized along with the physical and chemical surface properties of the synthesized nanoparticles.

#### NS-Contributed On Demand-7 Mechanical Size Effect of Nanoconfined Polymer Films, *Guorui Wang, F. Najafi, K. Ho, M. Hamidinejad, T. Cui, G. Walker, C. Singh, T. Filleter*, University of Toronto, Canada

The mechanical properties of polymer thin films are of scientific and technological interest to diverse communities of researchers. This interest is mainly driven by the development of flexible and stretchable electronics with a wide range of applications in flexible, wearable, and implantable devices. While the moduli of thin polymer films are known to deviate dramatically from their bulk values, the nature of such a size effect still remains debatable. Specially, indentation technique gives rise to contradicting results from both buckling experiments and molecular dynamics calculations, which is claimed to result from the substrate effect. Herein, we perform atomic force microscope (AFM)-based deflection testing on freestanding ultrathin polymethyl methacrylate (PMMA) films in confined geometry and demonstrate a significant mechanical stiffening behavior in the absence of substrate effect. Through a combination of

small-angle X-ray scattering (SAXS) and scanning near-field optical microscopy (SNOM) measurements, a transition in chain conformations was identified from bulk to ultrathin film which can be directly related to the mechanical behavior of the polymer films. Based on such a structure-property relationship, we advocate that individual chains play a critical role in polymer mechanics at the nanoscale. Molecular dynamics (MD) modeling further unveils the dominance of entropic contribution over enthalpic contribution to the chain stiffness, in terms of substantial conformational transition but limited backbone straining during the stretching, which endows polymer films with higher load bearing capacity and accounts for the stiffening of polymer films. In this context, stress states of chains account for the molecular origin of the mechanical size effect of polymer thin films. In particular, biaxial stretching of chains (e.g. from the AFM deflection test) leads to the stiffening due to the chain stiffness effect, while the compression/bending (e.g. from the wrinkling method) results in a softening behavior in terms of the flexibility of chains. In contrast to the conventional interchain interaction-dominated elasticity mechanism, such a mechanistic understanding resolves the long-standing issue regarding the discrepancy in the observation of thickness dependent modulus of polymer thin films.

#### NS-Contributed On Demand-10 In-Plane Mechanical Properties of 2D Hybrid Organic-Inorganic Perovskites Nanosheets by AFM Nanoindentation, *Doyun Kim*, Texas A&M University; *E. Vasileiadou, I. Spanopoulos, M. Kanatzidis*, Northwestern University; *Q. Tu*, Texas A&M University

In-plane mechanical strains are commonly found in 2D metal halide organic-inorganic perovskites (2D HOIPs) which have attracted substantial interests due to their chemical/structure versatility and high-performance optoelectronic applications such as solar cells, light emitting diodes and flexible electronics. Such mechanical strain in HOIPs due to thermo-mechanical, electro-mechanical or photo-mechanical coupling derives the delamination and fracture of the functional materials, resulting in catastrophic failure of the devices. In order to mitigate these strain-induced stability issues, it is crucial to understand the fundamentals of mechanical properties and their relationship to the composition and structure of the material. However, the current understanding of the in-plane mechanical properties of 2D HOIPs and the influence of their structure on the mechanical performance is limited. Here, we employed Atomic Force Microscope (AFM) indentation to stretch suspended 2D lead halide Ruddlesden-Popper HOIP nanosheets, systematically studying the in-plane Young's moduli  $E_{||}$ . The general formula is  $(R-NH_3)_2PbX_4$  where  $X = I, Br, or Cl$  and  $R-NH_3$  is linear alkyl ammonium spacer molecule  $(C_mH_{2m+1}-NH_3^+)$ ,  $m = 4, 6, 8$  or  $12$ ). With fixing the spacer molecule to butylammonium and varying halide ions, we found that the  $E_{||}$  follows the trend of Pb-X bond strength ( $Pb-Cl > Pb-Br > Pb-I$ ), which is different from that found in out-of-plane moduli  $E_{\perp}$  of HOIPs, but rather closer to that found in 3D counterparts. Moreover, the impact of the alkyl ligand chain length on  $E_{||}$  exhibits nonmonotonic dependence that decreases first and slightly increases again. This is likely due to the competition between the relative packing density of soft organics and the interfacial mechanical coupling associated with the packing of the alkyl chains. The mechanical anisotropy of 2D HOIPs can be tuned over a wide range ( $0.1 < E_{||}/E_{\perp} < 2$ ) by engineering the organic spacer molecules, especially for the iodide-based 2D HOIPs, which is significantly different compared to other inorganic 2D materials. Our results provide valuable insights into the structure-property relationship regarding the mechanical anisotropy and in-plane mechanical behaviors of 2D HOIPs, which can guide the materials design and device optimization to achieve required mechanical performance in 2D HOIP-based applications.

#### NS-Contributed On Demand-13 How does Humidity affect the Mechanical Behavior of Halide Perovskites?, *Isaac Buchine*, Bar-Ilan University, Israel; *I. Goldian, S. Cohen, D. Cahen*, Weizmann Institute of Science, Israel ABX<sub>3</sub> Halide Perovskites, HaPs, where A= Methylammonium (MA), Formamidinium (FA), or Cesium (Cs), B= Pb, X=Chloride (Cl), Bromide (Br), or Iodide (I), are promising materials for the next generation of semiconductor-based devices. Their facile fabrication alongside intriguing optoelectronic properties make them outstanding candidates for incorporation into a variety of next generation technologies.

The effect of humidity on HaP *optoelectronic properties* has been investigated thoroughly, but no studies exist on how it influences their *structural and mechanical integrity*, critical, because of the apparent central role of their mechanical softness for their other properties. In particular, the well-studied HaP out-of-plane mechanical properties, are

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known to depend strongly on the Pb-X bond, but the influence of humidity on this characteristic has been ignored until now. This presents a difficulty in engineering devices containing these materials meant to operate under a range of ambient conditions.

We examined single crystals of five HaPs, MAPbX<sub>3</sub> (X = Cl, Br, and I) and APbBr<sub>3</sub> (A = Cs and FA), to elucidate the role composition plays in the humidity-dependent mechanical properties. A dedicated nanoindenter, as well as an atomic force microscope-based approach, were used to measure elastic and plastic deformation under varying *in situ* humidity conditions. Furthermore, using temperature-dependent desorption we identified a tightly bound water species populating about one in eight unit cells in a FAPbBr<sub>3</sub> crystal which was stored in dry conditions.

Our results reveal that the elastic modulus (E) increases by 4-10% while the hardness (H) decreases by 25% when RH (relative humidity) is increased from 10% to 60%. This effect is reversible upon reverting to the dry state. The phenomenon is strongest in HaP crystals with cubic lattices (MAPbCl<sub>3</sub>, MAPbBr<sub>3</sub>, and FAPbBr<sub>3</sub>). HaP crystals with tetragonal lattices (CsPbBr<sub>3</sub> and MAPbI<sub>3</sub>) show negligible humidity dependence relative to experimental uncertainty. This suggests that lattice structure and dimensions play a critical role in the humidity-HaP relationship, an aspect not usually taken into consideration when discussing the function of these materials. Common knowledge in the field suggests that H-bonding is the primary source for humidity effects on HaP properties. However, our research suggests that the lattice that is stable at RT and atmospheric pressure and the available space within the unit cell affects these properties as well, and should be considered.

**NS-Contributed On Demand-16 Ultrathin, Stress-Free, Doubly-Clamped Nanomechanical Resonator, Jian Zhou, N. Moldovan, L. Stan, H. Cai, D. Czaplewski, D. López,** Argonne National Laboratory

Ultrathin mechanical structures are ideal building platforms to pursue the ultimate limit of nanomechanical resonators for applications in sensing, signal processing and quantum physics. As the thickness of the vibrating structures is reduced, the built-in stress of the structural materials plays an increasing role in determining the mechanical performance of the devices. Therefore, it is very challenging to create resonators working in the modulus-dominant regime, where their dynamic behavior is exclusively determined by the device geometry. Here we demonstrate the realization of ultrathin (nm thickness), high-aspect-ratio (L/t up to 5000), doubly-clamped nanomechanical resonators, with built-in stress in the kPa range. We show that the resonators have stiffness that scales with the device dimensions according to beam theory, as opposed to the magnitude of the built-in stress characteristic to a string. We observed room temperature thermomechanically induced motion more than ten vibrational modes with all the frequencies matching the calculations according to the beam theory, and a record frequency tuning range of more than 50 times by the application of  $\sim 1 \times 10^{-3}$  strain while retaining simple harmonic response of the resonator. These results illustrate a new strategy for the quantitative design of nanomechanical resonator with unprecedented performance.

**NS-Contributed On Demand-19 Thermal Activation of Nanoscale Wear, W. Wang,** Southwest Jiaotong University, China; **D. Dietzel, Andre Schirmeisen,** Justus-Liebig University Giessen, Germany

Macroscopic wear is routinely described by empirical laws like, e.g., the historic Archard's law, while the underlying microscopic processes are still under scientific debate. On the nanoscale the removal of single atoms from the sliding surfaces is considered the most fundamental mechanism of wear, also termed atomic attrition. Especially atomic force microscopy (AFM) techniques have been widely used to explore nanoscale wear in single asperity sliding scenarios, where material abrasion can be found for both the AFM tip and the substrate depending on the experimental conditions or material combinations.

In this work we have created nanoscale wear tracks on ionic crystals by reciprocating single asperity scratch tests using AFM. The wear characteristics are analyzed by the scratch depth as a function of surface temperature from 30 to 300 K. We find two distinct regimes of wear track formation: At low temperatures the wear groove volume shows a monotonic increase with contact time and temperature, fully consistent with the thermally activated Arrhenius kinetics. Above a certain temperature threshold, however, the wear tracks start to show a periodic wear pattern and the total wear volume becomes almost independent of temperature. This apparent contradiction can be understood if further competing processes are considered at high temperatures. These include surface diffusion and rebonding processes of the atomic wear debris, previously shown to be responsible for the formation of quasiperiodic

mound patterns. Finally, we show that with a proper wear mound volume correction even the high temperature wear data can be described by the simple Arrhenius model, indicating that the same atomic attrition process is responsible in both regimes. By linking these two regimes, our results hint at a path to predict nanoscale wear not only for smooth but also for rough surfaces, a further step toward realistic interfaces.

**NS-Contributed On Demand-22 Reduction in Contact Time of Bouncing Droplets on Compact Nanostructured Superhydrophobic Surfaces, Lin Wang,** Department of Materials Science and Engineering, Materials Research Institute, The Pennsylvania State University, University Park; **T. Wong,** Department of Mechanical Engineering, Materials Research Institute, The Pennsylvania State University, University Park

Many natural surfaces are capable of shedding water droplets rapidly, which has been attributed to the presence of low solid fraction ( $\Phi_s \sim 0.01$ ) according to the classical wetting theories. However, recent high-resolution microscopic observations revealed the presence of unusual high solid fraction nanoscale textures on water-repellent insect surfaces. For example, superhydrophobic mosquito eyes, springtails, and cicada wings possess solid fractions ( $\Phi_s$ ) as high as 0.25 – 0.64. In addition, the texture size on these insect surfaces is typically on the order of 100 – 300 nm. To understand why both high solid fraction and nanoscale textures are important for these superhydrophobic insect surfaces, we systematically designed and fabricated a series of textured surfaces with texture size varying from 100 nm to 30  $\mu$ m at solid fractions of 0.25 and 0.44, and investigated their static and dynamic wetting behaviors. Here we show that the contact time of bouncing droplets on high solid fraction surfaces can be reduced by reducing the texture size to nanometer scale. Specifically, we discovered that high solid fraction surfaces ( $\Phi_s \sim 0.44$ ) with texture size  $\sim 100$  nm could reduce the contact time by  $\sim 2.6$  ms compared to that with texture size  $> 300$  nm. This texture-size dependent contact time reduction on solid surfaces has not been observed previously, and cannot be explained by existing surface wetting theories. We showed theoretically that the reduction in droplet contact time can be attributed to the dominance of three-phase contact line tension on compact nanoscale textures. Through pressure stability analysis and experiments, we have further shown that high solid fraction ( $\Phi_s > 0.25$ ) is an important requirement for insects to withstand high-speed impacting raindrops. Our results suggest that the compact and nanoscale textures on water repellent insect surfaces may work synergistically to repel and shed impacting raindrops rapidly, which could be an important survival strategy for flying insects. Technologically, the ability of compact nanoscale textured materials to repel high-speed impact of liquid droplets with reduced contact time may find use in a range of applications including fouling-resistant personal protective equipment (PPE) to insect-sized flying robots and miniaturized drones.

Keywords: contact time | drop impact | insects | nanoscale textures | pressure stability | superhydrophobic surfaces

**NS-Contributed On Demand-25 Efforts of Interlayer Interaction on van der Waals Heterostructure Nanomechanical Resonators, Wen Sui, J. Lee, P. Feng,** University of Florida

Atomically thin membranes made of two-dimensional (2D) layered materials such as graphene and molybdenum disulfide (MoS<sub>2</sub>) have attracted considerable interests in enabling novel resonant nanoelectromechanical systems (NEMS) thanks to their superior mechanical properties (e.g., high Young's modulus,  $E_Y \approx 200$  GPa-1TPa, and ultrahigh strain limit, often up to  $\epsilon_{\text{limit}} \approx 25\%$ ). Various 2D NEMS resonators based on different crystalline materials have been demonstrated with great performance, including wide frequency tuning up to  $\Delta f/f_0 \approx 1300\%$ <sup>[1]</sup> and broad dynamic range up to  $\sim 110$  dB<sup>[2]</sup>.

Recently, van der Waals heterostructures based on stacking of atomically thin 2D crystals with disparate electrical, mechanical, and thermal properties have been proposed for the realization of new functional NEMS devices. Previous work in MoS<sub>2</sub>/graphene heterostructure NEMS resonator indicates that the resonance frequencies and Q factors of the heterostructure 2D resonators lie between the values of single-material resonators in graphene or MoS<sub>2</sub><sup>[3]</sup>. In such 2D heterostructures, interlayer slip may occur owing to the effects of twist, strain, or mismatch of lattice constants<sup>[4]</sup>. However, how the interlayer interactions affect the tension level, thermal expansion, and damping of heterostructure resonators is elusive and unexplored so far.

In this work, we investigate the performance of 2D NEMS resonators enabled by atomic layer MoS<sub>2</sub>/graphene van der Waals heterostructures with respect to temperature variations by using finite element method

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(FEM) simulations. We mainly focus on exploring the effects of stress softening, geometric changes, as well as the temperature dependence of material properties. Effects of thermal cycling on the interlayer interactions, especially how the interfacial bonding and/or the thermal expansion affect the nanomechanical characteristics of suspended MoS<sub>2</sub>/graphene resonators are systemically analyzed. This work opens possibilities for studying multi-physical coupling effects in 2D heterostructure devices by unraveling the interlayer interactions in van der Waals heterostructures.

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## NS-Contributed On Demand-28 Intrinsic and Interfacial Fatigue of Graphene, Teng Cui, T. Filleter, University of Toronto, Canada

The booming applications of graphene in flexible electronics, mechanical structures, and biomedical sensors require robust mechanical and structural properties as a premise. With the ever-increasing demand for the long-term reliability of graphene-based devices and structures in real applications, the fatigue behavior of graphene necessitates careful investigation, especially its intrinsic fatigue behavior and interfacial fatigue behavior at contact. The fatigue concern of graphene is more stringent under extreme loading conditions for more complicated designs, such as at severe stress concentrations and abundant interfaces in flexible devices. Here we enabled the intrinsic fatigue study of suspended two-dimensional (2D) materials based on a modified atomic force microscopy technique. We discovered [1] that monolayer and few-layer graphene also suffered mechanical fatigue, but they exhibited remarkable fatigue life of more than one billion cycles at large stress levels (e.g., at  $\sigma_{\text{mean}}=71$  GPa and  $\Delta\sigma=5.6$  GPa), which is higher than any materials reported to date. Surprisingly, monolayer graphene did not reveal any obvious progressive damage during cyclic loading, as manifested by its non-changing morphology and non-degraded mechanical properties, as well as atomic structures examination by molecular dynamics simulations. Graphene oxide, meanwhile, also exhibited ultrahigh fatigue resistance, but revealed clear progressive damage, similar to conventional fatigue mechanisms. Despite the record-high intrinsic fatigue life of graphene, we observed significant interfacial fatigue damage when introducing graphene-polymer contact [2]. The significant elastic mismatch and weak van der Waals (vdW) interactions at the interface resulted in the generation and propagation of graphene buckles, which was revealed to follow an inverse Paris' law. Moreover, cyclic loading through the vdW interfaces could also induce fracture of graphene even in tens of cycles, with the main fracture modes identified as in-plane shear at the fold junctions and tear. These studies provide fundamental insights on the dynamic reliability of graphene and call for further fatigue studies of other 2D materials and their interfaces.

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## NS-Contributed On Demand-31 Atomic-Scale Visualization of Electron-Pair Fluids and Crystals, Xiaolong Liu, Y. Chong, Cornell University; R. Sharma, University of Maryland College Park; J. Davis, Cornell University/University of Oxford/University College Cork

Translationally invariant electron pair fluids exist inside most conventional superconductors. However, electron pairs can also form crystalline states such as pair density waves (PDWs) that break translational symmetry. Experimental evidence of PDWs remains scarce due to the difficulty in

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directly visualizing the superconducting condensate. Herein, using atomic-resolution scanned Josephson-tunneling microscopy (SJTM), we show that PDW states exist in transition metal dichalcogenides, here NbSe<sub>2</sub>. Enabled by SJTM, we further visualized the velocity field and supercurrent density of a flowing electron-pair fluid on the surface of NbSe<sub>2</sub>. Such techniques are expected to find broad applications in other emerging quantum materials.

## NS-Contributed On Demand-34 High-Speed Scanning Tunneling Spectroscopy, Hamed Alemansour, S. Moheimi, University of Texas at Dallas; J. Owen, J. Randall, E. Fuchs, Zyvex Labs

Scanning tunneling microscope (STM) has been extensively used as an atomic-scale spectroscopy tool. One STM spectroscopy technique is current-imaging tunneling spectroscopy (CITS), i.e., recording I-V or dI/dV curves for every pixel of a topographic image. This offers a route to extract local electronic properties of surfaces. Implementation of CITS requires negligible lateral drift, low measurement noise, and a highly stable tip-sample junction. These requirements impose significant technical hurdles to increase the speed and precision of this technique and a map of a small area can take hours to be completed. We present a novel method to obtain I-V spectra for every pixel of an image under normal imaging speeds. Unlike the conventional approach, where the feedback loop is disconnected for every pixel and then the bias voltage is ramped over the desired range to record the tunneling current, we have developed a method to obtain I-V curves without the need to interrupt the feedback loop. Experimental requirements for this scanning tunneling spectroscopy (STS) method are easily fulfilled at room temperature. In this approach, a high-amplitude sinusoidal modulation voltage without a dc bias is generated by a lock-in amplifier and is applied to the sample. The resulting current that contains both tunneling and capacitive components is then amplified by a high bandwidth preamplifier. This is then sent to the lock-in amplifier that measures in-phase ( $a_1$ ) and 90° out of phase ( $b_1$ ) components of the current with the modulation signal. The natural logarithm of  $a_1$  ( $\ln(a_1)$ ) is compared with a set-point value and the error signal is sent to the controller. Similar to the constant current imaging mode, a topographic map of the sample is constructed by plotting the controller output along with the in-plane position of the tip. The tunneling current is also obtained by subtracting the capacitive current from the total current and I-V curves are constructed for every pixel, simultaneously with the imaging. This enables us to obtain a spectroscopic map of the surface hundreds of times faster than the conventional CITS method.

## NS-Contributed On Demand-37 Phonon Polaritons in New Materials for Nanophotonic Applications, Vanessa Breslin, D. Ratchford, U.S. Naval Research Laboratory; A. Giles, Quantitative Scientific Solutions, LLC; A. Dunkelberger, J. Owrutsky, U.S. Naval Research Laboratory

Phonon polaritons are collective nuclear charge oscillations resulting from the coupling of photons with optical phonons in polar materials and are supported within a material-specific spectral region called the reststrahlen band, which is bounded by the transverse and longitudinal optical phonons. In this region, the material behaves optically like a metal; it is highly reflective and has a negative real part of the permittivity. When polar materials are nanostructured, phonon polaritons can enable a variety of near-field optical effects such as sub-diffraction light confinement. Interestingly, a polar material which supports phonon polaritons can also have anisotropic optical properties, such that different components of its permittivity tensor have opposite signs. These materials are referred to as hyperbolic since, within the reststrahlen band, they behave optically like a dielectric and a metal along different crystal axes. Here, we report on the first observation of hyperbolic phonon polaritons (HPs) in calcite nanopillar arrays, demonstrate the aspect ratio dependence of the HP resonance frequencies, discuss fabrication challenges, and compare our results to numerical simulations and analytical models. Additionally, our efforts toward using calcite to demonstrate surface enhanced infrared absorption (SEIRA), a useful technique for chemical sensing applications, will be presented. Although plasmonic materials can be used for SEIRA, these materials typically suffer from high optical losses due to the fast scattering of electrons, which results in broad optical resonances. In contrast, phonon polaritons have much lower optical losses because of the slower scattering rates of phonons, resulting in narrower resonance bands. Therefore, calcite is an ideal low-loss material for studying HPs that could find applications in mid-IR nanophotonic devices, and these results pave the way for expanding the type of materials that support phonon polaritons.

**NS-Contributed On Demand-40 Nanoscale Chemical Analysis of Heterogeneous Amphiphilic Surfaces via Photo-Induced Force Microscopy, Derek Nowak, P. O'Reilly, Molecular Vista; J. Benda, C. Gu, D. Webster, North Dakota State University; S. Park, Molecular Vista**

Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) to achieve nanoscale chemical analysis via localized IR absorption spectrum and mapping of heterogeneous materials on the surface of a sample (with sub-10 nm spatial resolution). The exceptional spatial resolution is due to the tip-enhanced near-field profile, which extends  $\sim 10$  nm into the sample surface. In this talk, we present a slightly modified PiFM configuration where the technique becomes more bulk sensitive, which when combined with the surface-sensitive PiFM mode, allows a nanoscale "3-dimensional" analysis of a heterogeneous material system. We demonstrate the elegance and utility of the technique by analyzing amphiphilic siloxane-polyurethane (AmSi-PU) coatings, which have shown excellent fouling release properties due to the lateral phase separation and vertical stratification of the different constituent polymers [2]. The conclusions that are drawn from the PiFM measurements are compared with the conclusions that are drawn from multiple other techniques, which included ATR-FTIR, XPS, and AFM.

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**NS-Contributed On Demand-43 Controlled Electron-Induced Fabrication of Metallic Nanostructures on 1nm Thick Carbon Nanomembranes, C. Preischl, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany; Linh Hoang Le, Universität Bielefeld, Germany; E. Bilgillisoy, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany; F. Vollnhals, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany; A. Götzhäuser, Universität Bielefeld, Germany; H. Marbach, Friedrich-Alexander Universität Erlangen-Nürnberg, Germany**

Metallic nanostructures deposited on 2D materials are increasingly desirable for many electronic, magnetic and optical applications. Focus electron beam induced deposition (FEBID) is a direct and maskless lithography technique that operates based on irradiating precursor molecules by a focus electron beam of an electron microscope to dissociate them locally and then leave a metallic deposit.<sup>[1][2][3]</sup> Taking advantages of this technique, we could write highly pure iron patterns on a terphenylthiol self-assembled monolayer (SAM) with controlled shapes and sizes. Consequent crosslinking of the SAM under a low energy electron beam results in an insulate carbon network, which is well-characterized and known as carbon nanomembrane (CNM)<sup>[4]</sup>. This 1 nm thick membrane can be transferred on tertiary solid substrates, for example SiO<sub>2</sub>, or freely suspended on TEM grids, while the iron nanostructures are well preserved. This work has illustrated that the combination of FEBID and CNMs can be a promising route to obtain various metallic nanostructures with arbitrary designs embedded on mechanically stable and flexible ultrathin films.

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**NS-Contributed On Demand-46 Fully Motorized, Tip-Scanning AFM With Photothermal Excitation for Improved Imaging and Cell Measurement Methods, Jonathan Adams, C. Bippes, L. Howald, S. Fricker, P. Frederix, P. van Schendel, H. Gunstheimer, L. Gonzalez, G. König, Nanosurf AG, Switzerland; G. Fläschner, ETH Zurich, Switzerland; D. Ziegler, Nanosurf AG, Switzerland**

Atomic force microscopes (AFMs) are versatile tools that can effectively resolve structures and probe mechanical properties at length scales from nanometers to tens of micrometers, and in environments ranging from vacuum to biological solutions. Nevertheless, there is a strong continued need for AFMs with improved ease of use, reliability, and integration with complementary techniques. Recently, we have developed a new instrument, the DriveAFM, that combines a unique set of technological features for improved performance and ease of use. These include a tip scanning architecture that allows for flexibility over sample size and seamless integration with optical microscopy, fully motorized optomechanical adjustment that permits automation of many routine instrument adjustments as well as remote operation, and photothermal

excitation that excites cantilever oscillations in a straightforward and stable manner independent of environment.

In this work, we will illustrate how a novel optical guiding architecture overcomes the engineering challenges involved in incorporating these technological features in a tip scanning AFM. Our architecture allows for removing most optomechanical components from the scanner [1]. We will also highlight a range of new measurement and imaging modes that are enabled specifically through the incorporation of photothermal excitation. In comparison with piezoacoustic excitation, photothermal excitation can cleanly actuate the cantilever over a wide bandwidth of frequencies without influence of the surrounding environment or support structure [2]. The resulting clean phase response of photothermally-excited cantilevers allows for more accurate tracking of the cantilever resonance frequency, used in the PicoBalance technology which enables fast and accurate measurements of cell and particle mass [3]. Furthermore, direct off-resonance actuation of cantilever deflection through photothermal excitation allows for cell mechanical property measurements at a wide range of frequencies [4], and off-resonance imaging modes that run at higher detection frequencies in comparison with previous piezo-based approaches [5].

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**NS-Contributed On Demand-49 Effect of the Surroundings on the Controlled Manipulation of Individual Phenyl Groups, Omur Dagdeviren, C. Zhou, E. Altman, U. Schwarz, Yale University**

Scanning probe microscopy has made it possible to move molecules between surface sites at will while quantifying the potential energy barriers along the manipulation path as well as the energy landscape surrounding the molecule in its initial and final positions. To explore the practicality of these abilities as a novel pathway to exploring the interactions between molecules as bonds form and break in a catalytic cycle, we selected iodobenzene molecules on a Cu (100) surface as a model system. To this end, we first break the iodine atom from the benzene ring by applying a controlled bias voltage to form a phenyl group. Afterwards, a manipulation path is chosen along which the tip moves at constant but continuously reduced heights while recording the oscillation amplitude and phase phi with the microscope operated in our recently developed tuned-oscillator (TO) detection scheme [1]. To preserve the accuracy of recovered tip-sample interaction potentials and forces, we use oscillation amplitudes significantly larger than the decay length of the tip-sample interaction potential [2,3]. Here, we show how moving a phenyl away from the iodine atom reduces the energy barrier required to initiate motion with increasing distance, thereby disclosing the effect of local surface chemistry.

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**NS-Contributed On Demand-52 Atomic-Scale Study of the Degradation Process on Single-Crystal Perovskite Surfaces: From Ultra-High Vacuum to Ambient Pressures, Joong Il Jake Choi, Center for Nanomaterials and Chemical Reactions, IBS, Republic of Korea; M. Khan, School of Electrical Engineering, KAIST, Republic of Korea; Z. Hawash, Energy Materials and Surface Sciences Unit, OIST, Japan; K. Kim, Beamline Research Division, Pohang Accelerator Laboratory (PAL), POSTECH, Republic of Korea; H. Lee, Department of Chemistry, KAIST, Republic of Korea; L. Ono, Y. Qi, Energy Materials and Surface Sciences Unit, OIST, Japan; Y. Kim, School of Electrical Engineering, KAIST, Republic of Korea; J. Park, Center for Nanomaterials and Chemical Reactions, IBS, and Department of Chemistry, KAIST, Republic of Korea**

While organic-inorganic hybrid perovskites are emerging as promising materials for next-generation photovoltaic applications, the origins and the pathways of the instability of perovskites remain speculative. Herein, we employ ambient-pressure atomic force microscopy (AP-AFM) and ambient-pressure x-ray photoelectron spectroscopy (AP-XPS) to carry out surface characterization and atomic-scale analysis of the reaction mechanisms for methylammonium lead bromide (MA(CH<sub>3</sub>NH<sub>3</sub>)PbBr<sub>3</sub>) single-crystal surfaces in environments ranging from ultra-high vacuum (UHV) to ambient

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pressures. MAPbBr<sub>3</sub> single crystals grown in a solution process are mechanically cleaved at UHV to obtain an atomically clean surface. We observe surface inhomogeneity on the freshly cleaved MAPbBr<sub>3</sub> surface: the coexistence of MA-terminated layers with cubic layer heights, and full and partial coverage of PbBr<sub>2</sub>-terminated defective layers with lower layer heights. Consecutive topography and lateral force measurements in low pressure water ( $p_{\text{water}} \approx 10^{-5}$  mbar) show the creation of degraded patches that are one atomic layer deep, gradually increasing their coverage until fully covers the surface at water exposure of  $2 \times 10^6$  Langmuir. We observed high-friction perimeters of the degraded patches which are equivalent to MABr-flat surface where methylammonium ligand establish strong interaction to the AFM tip, enhancing local friction. We show that exposure to high pressure water ( $p_{\text{water}} = 0.01$  mbar) depletes the organic ligands from the surface of MAPbBr<sub>3</sub>, which leads to the formation of PbBr<sub>2</sub> clusters and Br-rich surface.

## NS-Contributed On Demand-55 Correlative Imaging With Chemical Identification and Mechanical Mapping at the Nanometer Scale, *Shuiqing Hu, M. Wagner, W. Wang, H. Mittel, C. Su*, Bruker Nano Surfaces Inc

Mid IR induced photothermal effects at the nanoscale established an unique method for nanoscale chemical characterization and identification. Combining with PeakForce Tapping™ mode, PeakForce™ IR have demonstrated as an effective method to achieve high resolution chemical mapping. However, due to interaction time limited by PeakForce Tapping™ duty cycle, the photothermal IR detection has a lower efficiency comparing to contact mode and Tapping™ AFM IR. In this paper, we discuss a new method significantly improving S/N using multiple pulse train synchronized to the peak force interaction timing. Instead of the traditional single pulse trigger, a multi pulse train excitation is deployed, causing responses of the high Eigen mode contact resonance of the cantilever. Photo-thermal induced PeakForce™ IR signal can be enhanced by the much increased quality factor of the high Eigen mode contact resonance. High frequency for these contact resonances also facilitates more pulses for each tip-sample interaction cycle, leading to higher efficiency excitation of the photothermal IR signals. With combined efforts, the S/N can be improved by more than a factor of 2. Additionally we have developed correlative imaging with simultaneous chemical identification and nanomechanical mapping at the nanometer scale. The value of these correlative imaging are demonstrated in various inhomogeneous materials with diverse mechanical properties.

## NS-Contributed On Demand-58 High-Speed Scanning Ion Conductance Microscopy (SICM) for Imaging Cellular Process, *Georg Fantner, S. Leitao, B. Drake, V. Navikas, A. Radenovic*, EPFL, Switzerland

Scanning ion conductance microscopy (SICM) is a non-invasive scanning probe technique where the topography of the sample surface is sensed via the flow of ions through a nano-capillary. This technique is particularly well suited for very soft samples such as living mammalian cells. As such, SICM would be ideal for time-lapse investigations of stemcell differentiation, virus infection, or membrane trafficking. However, traditionally SICM is a very slow technique, requiring hours for high-quality imaging. Based on techniques originally developed for high-speed AFM, we have built a high-speed SICM that increased the hopping rate by a factor of 50 and can record images within seconds to minutes. Using a custom sample heater and perfusion chamber we can image live cells for 24h with high temporal resolution. The system is combined with a super-resolution optical microscope for correlative SICM/super-resolution fluorescence imaging. We use this system to study melanoma cell differentiation and its response to drug treatments.

## NS-Contributed On Demand-61 Metasurface Lens Efficiency Improvement using Genetic Algorithm with Evolutionary Optimization, *David Czaplewski*, Argonne National Laboratory, USA; *H. Cai*, New York University; *S. Srinivasan, A. Martinson*, Argonne National Lab; *D. Gosztola*, Argonne National Laboratory, USA; *L. Stan, T. Loeffler, S. Sankaranarayanan*, Argonne National Laboratory; *D. Lopez*, national institute of Standards and Technology

Recently, metasurface lenses have drawn significant interest to replace macroscopic lenses in applications ranging from cellular phones to medical diagnostic equipment because of their extremely small footprint in the transmission direction. Metasurface lenses focus light by creating the phase profile similar to a Fresnel lens and typically follow two common designs: waveguide design and nanoparticle design. The waveguide design uses high aspect ratio structures to confine the light within the structure and create an effective index of refraction in a sub-wavelength region of the lens<sup>1,2</sup>. By varying the lateral dimensions of the waveguide, different

phase delays can be created, while each waveguide remains independent from their neighbors. The primary problem with the waveguide design is that the creation of the high aspect ratio structures does not use commercially available processes. The nanoparticle design consists of an array of sub-wavelength dimension nanocylinders. The magnetic and electric dipole moments of the structure are tuned through lateral dimensions to match with the incident wavelength of light, creating an antenna, with full phase control from 0 to 2p and near 100% transmission. Using arrays of nanoparticles, phase delays can be characterized for different radii of the cylinders and spacing between cylinders. The fabrication process used to create the nanoparticles is CMOS compatible. The primary limitation of the nanoparticle design is that the nanoparticles interact with their neighbors. This complicates the design process. Borrowing the phase profile from a Fresnel lens and creating a nanoparticle metasurface, light can be focused to the desired focal point. However, the efficiency is low at 30%. Therefore, we employ an inverse design method<sup>3</sup> using a genetic algorithm (GA) with evolutionary optimization to design a lens that achieves an efficiency of 60% when fabricated and measured. In this talk I will present the fabrication of the metasurfaces and the methodology used to characterize the lenses. I'll also introduce the GA that we used to optimize efficiency. I'll discuss future directions of this work.

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## NS-Contributed On Demand-64 THz Dynamics of Correlated Excitations in Moiré Superlattice, *Jun Xiao, C. Xia, A. Lindenberg*, Stanford University

The emerging twisted heterostructures based on 2D layered materials have opened a unique platform to explore exotic correlation physics and novel heterostructure optoelectronic devices at the atomically thin limit. The tunable Moiré potentials, arising from interlayer couplings, result in the emergence of various novel orderings such as Mott insulating phases, unconventional superconductivity, and Moiré excitonic phases. In particular, transition metal dichalcogenide heterostructures allow for optically-excited electrons and holes to reside in different monolayers and for trapping in the tens-of-meV Moiré potential, which is quite favorable for developing valleytronics, exciton condensation, and programmable quantum emitter arrays. Further progress along this direction requires a precise understanding of the formation of these Moiré excitons, and how such formation can be engineered by Moiré potentials and electron correlations.

Here we use ultrafast terahertz emission spectroscopy to probe interlayer charge transfer and other quasiparticle dynamics in several types of Moiré superlattice based on the transition metal dichalcogenides. With ultrafast visible and near-infrared laser pumping of these distinct Moiré superlattices, we observed nontrivial variations in the THz emission dynamics and spectroscopy. Experiments indicate such changes are closely associated with varying Moiré patterns and momentum mismatch conditions. Our findings advance the microscopic understanding of the correlated carrier formation dynamics in twisted heterostructures and hold great promise to advance the development of novel 2D optoelectronic devices.

## NS-Contributed On Demand-67 Combined Scanning Gate Microscopy and Light Excitation Measurements on Semiconductor Nanowires, *Yen-Po Liu, J. Fast, Y. Chen, M. Kumar*, Lund University, Sweden; *R. Zhe*, DESY, Germany; *R. Timm, A. Burke, H. Linke, A. Mikkelsen*, Lund University, Sweden

InAs nanowires with tailored axial InP segments have attracted significant interest for nanophotonic applications such as photovoltaics, lasers and photodetectors as well as fundamental studies of for example hot-carrier dynamics [1,2,3]. Local variable electrical gating is very useful for studies of nanowires [4] and in conjunction with light excitation could explore the influence of local carrier density and band bending variations on device performance. This combination is however yet to be applied to nanowire devices. We have created a combined scanning photocurrent, atomic force and scanning gate microscopy (SPCM, AFM, SGM) setup to measure both local geometry and response to local light and voltage sources. We have used this setup to investigate the electronic response to local illumination and local gating response of InAs nanowires with/without an axial 25 nm InP segment.

The SGM imaging clearly show the influence of a local gate on the current profile of the InAs/InP nanowire devices. By placing the tip in specific positions on the wire, the current through the nanowire is enhanced by an order of magnitude. Simulations of carrier transport through the nanowire system as a function of gating tip position are performed based on drift-diffusion modelling [5] and the specific system geometry (from AFM images). A qualitative agreement between experiment and simulations is observed, which aids understanding of the device behaviour. When the nanowire is optically excited, significant changes in the SGM data are observed. These observations are discussed both in terms of carrier excitation in the wire, as well as the influence of surface states that can trap free carriers and introduce long-term memory effects in the devices. In conclusion, we show that by combining SGM, AFM, SPCM and simulations, new insights into the dynamics of nano-optoelectronic devices can be gained.

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**NS-Contributed On Demand-70 Ultralow Friction of Magnetene, a non-van der Waals 2D Material, Peter Serles**, University of Toronto, Canada; A. Puthirath, Rice University; S. Yadav, C. Veer Singh, University of Toronto, Canada; P. Ajayan, Rice University; T. Filleter, University of Toronto, Canada Two-dimensional (2D) materials are known to create ultralow friction interfaces by reducing the energy dissipated during the sliding of a contact. While this is often attributed to van der Waals (vdW) bonding of 2D materials, it is known that nanoscale and quantum confinement effects can act to modify the atomic interactions of a 2D material producing unique interfacial properties. We demonstrate that the ultralow friction which is characteristic of graphene and other vdW materials can be achieved in magnetene, a non-vdW bonded 2D iron oxide ( $\text{Fe}_3\text{O}_4$ ). Upon exfoliation from its bulk ore, the friction force of 2D magnetene as determined by friction force microscopy is found to decrease by a factor of more than 3 presenting statistically similar friction to common benchmark vdW materials. This effect, however, is unique to magnetene and is not present in the chemically similar 2D hematene ( $\text{Fe}_2\text{O}_3$ ) or isostructural 2D chromiteen ( $\text{FeCr}_2\text{O}_4$ ).

This ultralow friction can be attributed to nanoscale and quantum confinement of magnetene in producing three predominant mechanisms. First, the exfoliated (110) plane presents the lowest potential energy corrugation of the five materials as determined by DFT calculations. Using the potential energy corrugation to calculate the Prandtl-Tomlinson ideal friction of these materials shows considerable relative agreement with experimental friction values further validating this mechanism.[1] Second, quantum well confinement of a material to 2D can alter valence states and reactivity by electron confinement to 2D. It is noted by x-ray photoelectron spectroscopy measurements that magnetene shows a decrease in iron valence from  $\text{Fe}^{2.66+}$  towards  $\text{Fe}^{2+}$  which corresponds with reduced frictionally-detrimental  $\text{OH}^-$  adsorbate compared to the other non-vdW 2D materials.[2] Third, forbidden phonon modes due to asymmetric soft surface bonding are noted in the Raman spectra of magnetene accompanied by a reduction in phonon modes parallel to the direction of sliding. Phononic friction is due to the damping of sliding energy by atomic collisions with parallel phonon modes[3] therefore the modified phonon modes of 2D magnetene lessen damping thus reducing the friction force.

These three mechanisms of exfoliation, quantum confinement, and asymmetric surface bonding all contribute to creating a nanomaterial with ultralow friction properties which does not rely on the vdWs nature of bonding. This study not only identifies the fundamental mechanisms for the appearance of ultralow friction in a non-vdW material, but also presents the starting point for the engineering of nanomaterial properties to produce optimized 2D material interfaces.

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**NS-Contributed On Demand-73 Nano-Mechanical Characterization of Organic Micro-Inclusions in Flint, Sidney Cohen, I. Rosenhek-Goldian**, Weizmann Institute of Science, Israel; T. Corrales, Technical University Federico Santa Maria, Brazil; F. Natalio, Weizmann Institute of Science, Israel; A. Cernescu, Neaspec, Germany

Flint is a siliceous sedimentary deep sea rock produced by marine bacterial activity within a chalky environment under anoxic conditions. During the rock formation process, bacteria are entombed inside a silica gel. Organic remnants are thus key to understanding the initial and subsequent environment of the rock, but are subject to degradation and percolation occurring over millions, or even billions of years. This greatly complicates attempts to glean information on the past biology and evolution of the organic content. Eocene flint is relatively young - 50 million years old - and despite the fact that its organic matter could give a hint at how organics in much older flint have evolved over the years, this aspect remains largely unstudied.

We have applied a combination of in-situ, nanocharacterization techniques to gain new insights on this problem. These efforts were directed toward organic micro-inclusions entrapped in the flint. In particular, we show that the mechanical response of this material is an important quantity that provides complementary and unique data amongst other nano-characterizations applied. The small size, thickness and irregular morphology of the organic micro-inclusions make it very difficult to accurately determine the mechanical properties. Such irregularities rendered nanoindentation measurements unreliable. Scanning probe-based contact resonance measurements, on the other hand, proved to be suitable and consistent for characterizing these inclusions. We found a value of 29 GPa for the storage modulus of the organic micro-inclusion, while modulus values for the surrounding stone, 78 GPa, were typical for flint. Independent techniques, including nano-IR, Tof-SIMS, micro-Raman and EDS analysis, hint at a proteinaceous material (amine IR peak), yet this modulus is surprisingly high for a protein species in (the spectroscopically-determined) alpha-helix conformation. The micro-inclusion was further studied by exposing it to liquid water, which caused measurable swelling, and a strong decrease of the modulus. Both of these changes were reversible upon dehydration. The modulus in this case was measured using peak-force quantitative mechanical measurement. In this talk, the correlation amongst these different types of data will be presented to derive a full picture of these ancient organic pools. Strongly relying on the data from the nanoscale measurements, we propose that the pool is consistent with proteins and a mixture of diagenetic products.

Here we present the application of quantitative scanning probe-based mechanical measurements on ancient organic pools found inside flint. Despite their small and irregular size, as well as the rough morphology of these inclusions, these measurements have proven to be valuable, in situ techniques for determining the mechanical characteristics of flint. This approach, based on a suite of nanoscale techniques including the first quantitative nanomechanical measurements in this specialized geological context, describes a fresh approach to a (very) old problem.

**NS-Contributed On Demand-76 Mechanical Properties of Fibrillar Materials: The Role of H-Bond Formation in Amyloid Peptides, Irit Rosenhek-Goldian, N. Aggarwal, D. Eliaz, H. Cohen, S. Cohen, A. Kozell, T. Mason, U. Shimanovich**, Weizmann Institute of Science, Israel

The process of protein self-assembly into fibrillar structures generates the strongest biomaterials in the world, like silk fibers, but, unfortunately, is also associated with the development of neurodegenerative diseases.

Hydrogen bonds (H-bonds) are particularly important for proteins and natural peptides. They provide an organization guide for distinct protein folds, conferring stability to the protein structure and enabling specificity for selective inter- and intramolecular interactions.

Here, we describe a general approach for understanding the role of H-bonds in the protein self-assembly process on the fibril's exceptional mechanical properties. A series of peptides were studied in order to investigate the influence of substitution of an aliphatic amino acid by an aromatic one. These variations cause perturbations to the H-bonded

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network, that control the morphology and molecular structure of the formed fibers in a rational way.

Mechanical and morphological measurements conducted with AFM suggest that such changes severely affect the folds and fibrillation pathway in the mature solid state of the fibrils. This enables the manipulation of the end-point structure and the mechanical properties of fibrillar proteins, leading to Young's modulus alterations. When the peptides arrange in a globular structure they display relatively low modulus values of <7 GPa. fibrillar peptide assemblies show increased elastic modulus values ranging between 10 – 29 GPa, with the presence of aromatic amino acids contributing to improved stiffness. Amino-acid hydrophobicity and its propensity toward H-bond formation play a crucial role in the structural organization of peptide assemblies and in the rigidity of the formed structures. We show that steric hindrance, achieved via aliphatic-to-aromatic amino acid substitution, does not affect the natural propensity of the peptides to form amyloidogenic fibrils. These perturbations, however, do trigger changes in H-bonded network and conformational changes. These results are supported by structural and compositional analyses, electron diffraction, FTIR and quantitative XPS.

The approach presented here promotes a general understanding of the role of H-bonds in protein aggregation and opens the opportunity to utilize amyloidogenic protein fibrillation phenomena in rational material design.

## NS-Contributed On Demand-79 A Novel Experimental Method for Characterising Nano Insulating Materials (NIM) And Infill Gases, *Ofasa Abunumah, P. Ogunlode, E. Gobina*, The Robert Gordon University, UK

Nano Insulating Materials (NIM) are useful materials for thermal control in systems, such as buildings and endothermic reactions processes. NIM possess nanopores that could contain rarefied gases that would aid or inhibit the insulation quality across thermal boundaries. The coupling of quantities interactions, such as the matrix's and gas's thermal conductivities, flow due to thermal (creep coefficient) and pressure gradients (bulk modulus), with NIM matrix micro and macro surface boundaries present design and manufacturing opportunities and challenges for NIM, instrumentations devices, and infill gas selection. Therefore, understanding these surface interactions occurring in vacuum or rarefaction gas dynamics is important to engineers and facilitates the effective design and application of NIM in domestic and industrial processes. Some authors have analytically investigated the insulating quality of NIM using rarefied gas flowrate, but none has investigated the opportunities of using gas mobility to characterize the insulating quality of NIM vis-à-vis low pressure and low-high thermal gradients. Hence the motivation for this study. Gas mobility is a combinatorial quantity that couples nanomaterial (permeability) and fluid (viscosity) properties, therefore making it an elite engineering quantity to potentially characterize NIM insulating quality. Thus, this work aims to provide a novel method for characterizing NIM systems using gas mobility.

### Methodology and Materials:

An empirical approach involving gas experiments in nanoscale porous media was adopted for this study. Low pressures (0.20 – 1.00 atm), high temperature (up to 673K) were set as the working conditions. 5 analogous NIM core samples of varying structural parameters (macro surfaces-114, 118, 124, 300, and 524; pore size- 15nm, 200nm, and 6000nm; porosity- 3%, 4%, 13%, 14%, and 20%; and aspect ratios- 4.5E-05, 8.0E-05, 1.6E-03, 1.9E-02, and 3.4E-02) and 4 common industry gases (CH<sub>4</sub>, N<sub>2</sub>, Air and CO<sub>2</sub>) were the major materials used.

### Experimental Results:

A total of 3,600 data points from 1,200 experimental were used for various analyses. The research was able to characterize NIM systems using gas mobility, industry criteria, such as Knudsen and Reynold's numbers, and gas laws, such as Boyles and Charles laws. Unlike flow rates, mobility responses to pressure and thermal gradients were very low. It was observed that gas thermal/insulating interactions with the micro and macro boundary surfaces of NIM, as measured by mobility, was heightened as pressure increases from 0.20 to 1 atm, this was further validated by the improved correlation values (R<sup>2</sup>). CH<sub>4</sub> was found to be the most responsive to pressure and thermal boundary disturbances in NIM, while CO<sub>2</sub> is the least. Therefore suggesting that a NIM filled with CO<sub>2</sub> gas offers better insulating quality than the other gases.

### Contribution to Practice and Knowledge:

The multivariable (conditions, properties and parameters) settings to optimize mobility and the consequent optimal NIM system has been presented in detail. The merits and demerits of mobility-driven NIM

analysis and decision making were highlighted. The outcome would find direct utility and practical application in NIM and instrumentation device manufacturing, and infill gas selection.

**Keywords:** Nano Insulating Materials, creep coefficient, mobility, bulk modulus, gas, nanotechnology

## NS-Contributed On Demand-82 Realizing Gapped Surface States in the Magnetic Topological Insulator MnBi<sub>2</sub>SbTe<sub>4</sub>, *Wonhee Ko*, Oak Ridge National Laboratory; *M. Kolmer*, Ames Laboratory; *J. Yan, A. Pham, M. Fu*, Oak Ridge National Laboratory; *F. Luepke*, Forschungszentrum Jülich GmbH, Germany; *S. Okamoto, P. Ganesh, Z. Gai, A. Li*, Oak Ridge National Laboratory

MnBi<sub>2</sub>Te<sub>4</sub> is one of the most promising candidates of intrinsic magnetic topological insulators (MTIs) that displays nontrivial band topology with an intrinsic antiferromagnetic state. However, there are inconsistent observations on the existence of the exchange gap of MnBi<sub>2</sub>Te<sub>4</sub>, partially due to the highly electron-doped nature of the MnBi<sub>2</sub>Te<sub>4</sub> crystals and local inhomogeneity caused by the native defects. Here, we tailor the material through Sb substitution to shift the Fermi level into the bulk band gap and utilize scanning tunneling microscopy (STM) to assess the electronic structure and its local disorder. Quasiparticle interference and four-probe transport measurements displayed the surface states with a band gap of 50 meV for MnBi<sub>1.36</sub>Sb<sub>0.64</sub>Te<sub>4</sub> (MBST). The surface band gap is robust against the out-of-plane magnetic field despite the promotion of field-induced ferromagnetism detected by in situ magnetostriiction measurement. However, atomic defects significantly affect the surface band gap by shifting the bands. The results indicate that further optimization of the defects in bulk-insulating MBST will offer a promising platform for exploring emergent topological phenomena. This research was performed at the Center for Nanophase Materials Sciences which is a DOE Office of Science User Facility.

## NS-Contributed On Demand-85 Statistical Detection of Josephson, Andreev, and Single Quasiparticle Currents in Scanning Tunneling Microscopy, *Wonhee Ko, E. Dumitrescu, P. Maksymovych*, Oak Ridge National Laboratory

The tunnel junction between superconductors is the heart of many modern quantum information devices, such as superconducting qubits realized from quantum resonators with Josephson junctions. However, several tunneling mechanisms occur simultaneously in the superconducting tunnel junction, and thermal broadening further mixes them to obscure the identification of the tunneling mechanism. Here, we present a method to identify distinct tunneling modes in a tunable superconducting tunnel junction composed of superconducting tip and sample in a scanning tunneling microscope, specifically the one made of a Pb coated tip on a Pb single crystal. Combining the measurement of the relative decay constant of the tunneling current extracted from *I-V-z* spectroscopy with its statistical analysis over the atomic disorders in the sample surface, we identified the crossover of tunneling modes between single quasiparticle tunneling, multiple Andreev reflection, and Josephson tunneling with respect to the bias voltage even at a measurement temperature nearly half of the critical temperature. This method enables one to determine the particular tunneling regime independently of the spectral shapes, and to reveal the intrinsic modulation of Andreev reflection and Josephson current that is crucial for quantum device application of superconductors.

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

## NS-Contributed On Demand-88 Nanomaterial Adhesion Depends on Specific-Ion Effects Within Common Reservoir Fluids, *H. Chen*, Aramco Services Company - Boston; *S. Eichmann*, Aramco Services Company - Houston; *Nancy Burnham*, Worcester Polytechnic Institute

More efficient oil extraction would lower the need for environmentally risky infrastructure as well as lower the price of oil-based consumer products. Nanomaterials are used as tracers in oil-field characterization, for which minimal adhesion between the nano-tracers and rock (e.g. calcite) surfaces is desired. Building upon earlier experimental work, in which the tip of an atomic-force microscope (AFM) stood as a surrogate for a nano-tracer [1], we investigate the effects of i) ambient fluids typical of oil reservoirs and ii) surface defects using steered molecular dynamics simulations [2,3]. Media used to improve oil extraction include both fresh water and seawater. In our simulations, deionized water, salt-doped water ("seawater"), and calcium-doped seawater ("brine") were used as the fluids surrounding a carboxyl-terminated AFM tip above a defect-free calcite surface and also above both line and point defects on a calcite

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surface. As determined earlier [2], calcium ions preferentially bound to the calcite and carboxyl groups lowered the adhesion in calcium-doped fluids. Adhesion magnitudes of line and point defects were distinct in deionized water, with an average adhesion of  $(2.51 \pm 0.78)$  nN. In comparison, in seawater the overall adhesion magnitudes remained similar to those of deionized water,  $(2.52 \pm 0.75)$  nN, although their differences within seawater were generally no longer statistically significant. As for brine, the differences in adhesion among the defects were also generally no longer significant. However, the average adhesion magnitude of  $(1.27 \pm 0.63)$  nN was markedly lower in brine than for the other two fluids. These results help understand nano-tracer sticking mechanisms and could improve the extraction of oil.

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## NS-Contributed On Demand-91 Walking the Plank: Solar Cell Nanowire Arrays Probed *in situ* by Surface Potential Microscopy, Austin Irish, L. Hrachowina, R. Timm, Lund University, Sweden

Nanostructured III-V semiconductors have brought third generation photovoltaic devices to the brink of mass application. InP nanowire arrays have already demonstrated excellent performance, offering high efficiency and low cost. Perfecting device fabrication and performance will require intimate knowledge and utmost control over the semiconductor nanosurfaces. We present an *in situ*, cross-sectional Kelvin probe AFM technique for measuring nanowires within the array along their axis. Whereas alternative methods involve destructively removing nanowires from their growth substrate, we keep the structures intact and on their original growth substrate. This ensures relevance and precision while probing *p-n* junction surfaces. Ambiently measuring arrays gives timely feedback for subsequent processing. Selectability allows comprehensive single-nanowires characterization when combined with other electronic/spectroscopic techniques (e.g. EBIC).

## NS-Contributed On Demand-94 Probing Interfacial Properties of Iron Oxide Thin Films on Noble Metal Substrate by Scanning Tunneling Microscopy, Dairong Liu, J. Schultz, University of Illinois at Chicago; S. Mahapatra, University of Illinois at Chicago, India; N. Jiang, University of Illinois at Chicago, China

For the past several decades, scanning tunneling microscopy (STM) has enabled the atomic resolution study of the morphology and electronic characteristics of surfaces, including molecular adsorbates. However, the lack of chemical information critically limits its ability to fully define atomic environments. In contrast, optical spectroscopy is widely used to study the highly sensitive vibration fingerprints of chemical species. By combining STM with Raman spectroscopy, tip-enhanced Raman spectroscopy (TERS) can spectroscopically define interactions and chemistry at the spatial limit. This work highlights our investigations of subnanoscale surface structure. TERS enabled us to precisely probe molecule–molecule and molecule–substrate interactions at the nanoscale, such as distinguishing the packing model of subphthalocyanine (SubPc) on Ag(100) and discerning the localization of a subtle molecule–substrate interaction within the structure of a molecule. By pushing the spatial resolution below the level of nanoscale self-assembled molecular islands, TERS was found to offer the unambiguous characterization of molecular binding conformations and orientations that result in unique self-assemblies of rubrene with 5 Å spatial resolution. In order to address potential tip-related issues, we used Ar<sup>+</sup> ion sputtering of TERS probes, providing a method to recycle and preserve the plasmonic probes under UHV conditions, thus enabling their continued use for >2 months. This method further contributes to the implementation of TERS in different laboratories. In conclusion, these works develop TERS towards the study of highly localized inter-molecular interactions, which indicate the promising future of TERS in surface science research.

## NS-Contributed On Demand-97 Room Temperature Spin Transport in Cd<sub>3</sub>As<sub>2</sub>, Gregory Stephen, A. Hanbicki, Laboratory for Physical Sciences; T. Schumann, University of California at Santa Barbara; J. Robinson, Naval Research Laboratory; M. Goyal, University of California at Santa Barbara; S. Stemmer, University of California Santa Barbara; A. Friedman, Laboratory for Physical Sciences

As the physical limits of CMOS loom closer, alternative state variable paradigms become increasingly important. Devices utilizing the electron spin as a state variable are especially promising due to their intrinsic non-volatility, speed, and versatility. Fully incorporating spintronic devices into next-generation computing systems requires optimized architectures and materials capable of efficiently harnessing the electron spin. One particularly promising class of materials are topological Dirac semimetals (TDS), exemplified by Cd<sub>3</sub>As<sub>2</sub>. TDS materials have high mobilities, 3D Dirac cones, and can exist in multiple quantum phases. We demonstrate the function of Cd<sub>3</sub>As<sub>2</sub> as a channel for the flow of spin currents by incorporating it with hybrid graphene/MgO tunnel barriers as a non-local spin valve, the basic unit of spintronic devices for logic operations. We show that the spin valves operate at least up to room temperature. [1] We quantify the spintronic transport in the devices by measuring the spin Hall effect/inverse spin Hall effect, observing spin Hall angles up to  $\theta_{SH} = 1.5$  and spin diffusion lengths of 10–40 μm. Long spin-coherence lengths with efficient charge-to-spin conversion rates and coherent spin transport up to room temperature, as we show here in Cd<sub>3</sub>As<sub>2</sub>, are enabling steps toward realizing practical spintronic-based computing systems.

[1] G. M. Stephen *et al.* ACS Nano **15**, 5459 (2021).

## NS-Contributed On Demand-100 Reconstructing the Intrinsic Potential Energy Landscape of Interfacial Interactions With Thermally Modulated Force Spectroscopy, Alan Liu, T. Sulchek, Georgia Institute of Technology

Force probes are powerful experimental tools to measure the strength and physical extent of interfacial and intermolecular interactions at nanometer scales. However, because of the stochastic nature of force measurements, most force spectroscopy models require massive quantity of data in order to obtain meaningful energetic information of the interaction. We developed a force spectroscopy framework based on thermally modulated atomic force microscopy (AFM) force measurements capable of reconstructing energy landscapes of interfacial interactions over 100 nm distances from a handful of force curves. To address the challenge of insufficient sampling at the key points of the interactions, we defined exact equilibrium forces to serve as fiduciary markers that can be used to reliably overlay repeated force curves. The equilibrium force markers create a major advantage in that multiple under-sampled force measurements can be compiled as one fully sampled measurement of key regions of two state binding. We experimentally demonstrate the application of the method to find the intrinsic, continuous force and energy landscape reconstructed along an unprecedented 100 nm distance from merely 15 AFM force curves.

## NS-Contributed On Demand-103 Open-Loop Amplitude-Modulation Kelvin Probe Force Microscopy Implemented in Single-Pass Peakforce Tapping Mode, Gheorghe Stan, P. Nambodiri, National Institute of Standards and Technology

Over many years, an abundance of developments and applications has made Kelvin probe force microscopy (KPFM) one of the most versatile nanoscale surface electronic characterization techniques. In the last years, significant developments were made to make KPFM faster, with direct measurement for the tip-sample contact potential difference (CPD), and free of feedback constrains. For example, the open-loop (OL) variants of KPFM provide access to the voltage response of the electrostatic interaction between a conductive AFM probe and the investigated sample. The measured response can be analyzed *a posteriori*, modeled, and interpreted to include various contributions from the probe geometry and imaged features of the sample. In contrast to this, the current implemented closed-loop (CL) variants of KPFM, either amplitude-modulation (AM) or frequency-modulation (FM), solely report on their final product in terms of the tip-sample contact potential difference. In ambient atmosphere, both CL AM-KPFM and CL FM-KPFM work at their best during the lift part of a two-pass scanning mode to avoid the direct contact with the surface of the sample. To address few of these impediments, we demonstrate here a new OL AM-KPFM mode implemented in the single-pass scan of the PeakForce Tapping (PFT) mode. The topographical and electrical components were combined in a single-pass by applying the electrical modulation in between the PFT tip-sample contacts, when the AFM probe separates from the sample. In this way, any contact and

tunneling discharges are avoided and, yet, the location of the measured electrical tip-sample interaction is directly affixed to the topography rendered by the mechanical PFT modulation at each tap. Furthermore, because the detailed cantilever's response to the bias stimulation was recorded, it was possible to analyze and separate an average contribution of the cantilever to the determined local contact potential difference between the AFM probe and the sample imaged. The removal of this unwanted contribution greatly improved the accuracy of the AM-KPFM measurements to the level of the FM-KPFM counterpart.

**NS-Contributed On Demand-106 Strain-modulated Electronic Properties in Epitaxial FeSn Thin Films on SrTiO<sub>3</sub>(111),** *Huimin Zhang, Q. Zou, West Virginia University, USA; M. Weinert, University of Wisconsin, Milwaukee,; L. Li, West Virginia University, USA*

The crystal structure of FeSn consists of alternating Fe<sub>3</sub>Sn Kagome and Sn honeycomb lattices, which provides a versatile platform for correlated topological phases hosting symmetry-protected electronic excitations and magnetic states. To date most work on FeSn was carried out on cleaved bulk materials. Here, we synthesize high quality FeSn thin films on SrTiO<sub>3</sub>(111) substrates by molecular beam epitaxy. The growth mode is found to be 3-dimensional, and x-ray diffraction confirms single crystalline FeSn structure. Using low temperature scanning tunneling microscopy/spectroscopy, we observe perfect honeycomb lattice on the surface of the islands for film thickness above 10 nm, characteristic of Sn-termination. For film thickness less than 10 nm, periodic stripes due to distortion of the honeycomb lattice is observed, indicative of strain. On the deformed honeycomb lattice, we find enhanced local density of states at  $E = -0.3$  eV. We also observe various types of defects such as Fe anti-site and vacancy defects, which also modulate the electronic properties of FeSn. Our results demonstrate strain-controlled electronic properties in a Kagome magnet, key to developing its potential applications in future spintronic devices.

This research is supported by NSF (EFMA-1741673).

**NS-Contributed On Demand-109 Structure-Function of PC Surfactants,** *Nir Kampf, W. Lin, J. Klein, Weizmann Institute of Science, Israel*

Surfactants are surface-active materials that act as carriers and boundary lubricants. We compared the surface structure and function of three types of highly hydrated monomeric-, oligomeric- and di-block copolymer- based phosphocholine (PC) micelles. The AFM study under the surfactant solution showed that C<sub>16</sub>PC and oligo-methacryloyl(dodecylphosphorylcholine) surfactants are organized in a worm-like micelles structure on the mica surface. On the other hand, di-block copolymer, poly(n-butyl methacrylate-b-2-methacryloyloxyethyl phosphorylcholine), PBMA-b-PMPC has a globular structure on the mica surface with a typical diameter of about 20-40 nm. Friction measurements across the surfactants solutions using a Surface Force Balance technique demonstrate that monomeric or oligomeric surfactants show superior friction (friction coefficient,  $\mu = 10^{-3}$ ), with higher robustness of the latter, up to at least 5 MPa. Due to its lower surface coverage, the PBMA-b-PMPC surfactants was less efficient as boundary lubricant. We conclude that multimeric PC-surfactants may provide highly-stable, robust micellar boundary layers with excellent lubrication properties in aqueous media to high contact stresses.

**NS-Contributed On Demand-112 Selective Work Function Metal Etch Enabling Multi-V<sub>t</sub> Patterning for High Performance Stacked Nanosheet Devices,** *Curtis Durfee, IBM Research; S. Kal, TEL; M. Bhuiyan, S. Pancharatnam, IBM Research; M. Flaugh, I. Otto, TEL; H. Zhou, M. Belyansky, IBM Research; A. Mosden, TEL; N. Loubet, L. Meli, IBM Research; P. Biolsi, TEL; B. Haran, IBM Research*

Stacked gate-all-around nanosheet (GAA NS) device architecture provides the capability to co-integrate a wide range of channel width ( $W_{NS}$ ), enabling simultaneous low-power and high-performance applications on a single chip [1-8]. This architecture creates the ability to fine tune  $V_t$  independently for nFET and pFET devices by using the work function metal (WFM) layers as sacrificial "patterning" layers. Furthermore, reducing the vertical space between the Si channels ( $T_{SUS}$ ) will provide additional improvement in the device performance [4,7]. However,  $T_{SUS}$  scaling imposes significant integration and process challenges with High-K Metal Gate (HKMG) formation and WFM patterning [6, 7]; the traditional WFM wet etch solutions used for FinFET devices are insufficient to fully etch the pinched-off sacrificial layers between the Si channels for wide sheets ( $W_{NS}=100$ nm) due to the high aspect ratio [4], and to simultaneously stop on the desired layer for narrow sheets ( $W_{NS} = 20$ nm) due to low selectivity. This severely limits the etch options for WFM patterning in NS devices with wide sheets and scaled  $T_{SUS}$ .

In this paper, we present a highly-selective dry etch process which completely etches sacrificial pFET WFM metal for wide nanosheets ( $W_{NS} = 100$ ) from  $T_{SUS} = 9$  nm to extreme  $T_{SUS} = 5$ nm (Fig. 1) without any damage to the underlying HK HfO<sub>2</sub> surface. Etch selectivity to HK and etch dependence with anneals on doped and undoped layers were characterized on blanket substrates. The dry etch process also was qualified on integrated structures using structural and electrical tests. We selectively removed pinched-off pFET WFM in the nFET regions and re-deposited the full nFET WFM stack around the HK material that envelopes the Si channel, as shown in Fig. 2. This technique enables multi- $V_t$  patterning of nFET and pFET devices within the chip. M1 test results showed similar  $V_t$ , VBD, BTI at EOL and BTI slope for samples created with this technique and samples with "as-deposited" direct nFET WFM stack deposition (Fig. 3, 4). However, the wet etch process was self-limited; remaining pFET WFM prior to redeposition of the final nFET WFM caused degradation in  $V_t$ , VBD and BTI on wide sheets. There was no significant  $V_t$  degradation or variability across various  $W_{NS}$  from dry etch, indicating complete and selective etch of the pFET WFM.

We successfully demonstrated a gas phase WFM etch on stacked GAA NS devices. This novel isotropic and highly-selective etch capability is critical in facilitating WFM patterning, which enables multi- $V_t$  tuning and further device performance improvement with  $T_{SUS}$  reduction in high performance scaled NS logic devices [7,8].

**NS-Contributed On Demand-115 Cooperative Effects in DNA Nanofabrication,** *J. Majikes, P. Patrone, A. Kearsley, National Institute of Standard and Technology; M. Zwolak, National Institute of Science and Technology; J. Alexander Liddle, National Institute of Standard and Technology*

The Watson-Crick based pairing that enables sequence recognition and binding in DNA has been exploited in a variety of self-assembly schemes to build a diverse array of nanostructures. Although conceptually simple for single base pairs, the fabrication of DNA constructs can involve thousands of hybridization events, resulting in changes in enthalpy, entropy, and heat capacity that dictate the yield of the self-assembly process. The picture is further complicated by the fact that the energy scales relevant for DNA nanostructure assembly are on the order of  $kT$  at room temperature. This is essential for DNA's biological functionality but makes it difficult to engineer an assembly pathway to yield a target structure with high fidelity. We have worked to understand the self-assembly of DNA in the context of DNA origami, perhaps the most accessible and effective nucleic acid nanostructure fabrication methods [1]. In a typical origami system, 200 staple strands (oligomers  $\approx 30$  bases long) hybridize with a long ( $\approx 7000$  bases) scaffold strand to form the completed structure. Each staple typically has three binding sites, each of which can exist in open, bound, or blocked states. An almost infinite number ( $3^{600}$ ) of possible configurations may be explored during assembly. However, insight may be gained by examining what happens during a single staple-binding and strand-folding event. Using a novel affine transformation approach [2], we extract accurate and precise values of thermodynamic quantities from high-throughput fluorescent melt-curve experiments. Exploring a range of parameters, including staple strand concentration, change in scaffold strand topology on folding, and staple binding domain size, we quantify entropic effects [3] and identify a "blocked" state in which two related binding sites on the scaffold are each occupied by a staple, preventing a single staple from binding to both domains and creating a DNA origami fold. The blocked state becomes more likely for a single fold as the concentration of staple strands is increased. However, complete origami fold with high yield at high relative staple strand concentrations. This observation suggests that origami assembly is a result of a nucleation and growth process, following well-defined pathways in which each folding event strongly favors the occurrence of the next. We discuss our current understanding of cooperativity in self-assembly and its implications for nucleic acid nanostructure design.

[1] P. W. K. Rothmund, *Nature*, **440**, 297 (2006)

[2] P. N. Patrone *et al.*, *Analytical Biochemistry*, **607**, 113773 (2020)

[3] J. M. Majikes *et al.*, *Nucleic Acids Research*, **48**, 5268 (2020)

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## Nanoscale Science and Technology Division Room On Demand - Session NS-Invited On Demand

### Nanoscale Science and Technology Invited On Demand Session

**NS-Invited On Demand-1 Engineering Quantum Forces and Torques, Jeremy Munday**, University of California, Davis **INVITED**

The quantum vacuum gives rise to many effects that would not occur classically. One example is that the confinement of quantum electromagnetic fluctuations between two, isotropic macroscopic objects results in a force, i.e. the Casimir force. This force depends on both the geometry and the optical properties of the materials involved. An additional effect has been predicted for optically anisotropic materials, which can cause a rotation, i.e. a Casimir torque. Here we present our recent measurements of both of these phenomena. First, I will describe our results pertaining to the Casimir force between two spheres – a geometry that has previously eluded measurement due to experimental difficulties. Second, I will discuss additional geometries including pillars and holes that are now possible with this measurement technique and why they are interesting. Finally, I will conclude with a discussion of our recent measurement of the Casimir torque.

**NS-Invited On Demand-13 Visualizing Inside of 3D Self-Organizing Systems by 3D-AFM, Takeshi Fukuma**, Kanazawa University, Japan **INVITED**

Recently, three-dimensional atomic force microscopy (3D-AFM) has been proven to be a powerful tool for investigating various structures and phenomena at solid-liquid interfaces. In the method, a tip is scanned in the XY and Z directions in a 3D interfacial space. During the tip scan, the variations in the force applied to the tip is recorded to produce a 3D force image. At a solid-liquid interface, the tip interacts with surrounding solvent molecules during the tip scan. Thus, the obtained 3D image represents the distribution of solvent molecules. So far, the method has been used for visualizing 3D hydration structures on minerals, organic thin films, and biological systems with subnanometer-scale resolution. This emerging technology has attracted attention due to its potential applications in the research on interfacial control technologies for anti-fouling, lubrication, anti-freezing, colloidal dispersion, cosmetics and cleaning.

In the meanwhile, here I would like to draw attention to another important implication of the success of the 3D hydration measurements. In the AFM community, it has been a common sense that we should fix atoms or molecules to a solid surface to visualize them with atomic or molecular resolution. However, 3D-AFM allows us to visualize subnanometer-scale distribution of mobile water molecules that are not fixed on a solid surface. This is a big surprise and may lead to the breakthrough for the aforementioned limitation of AFM. Then, the next question would be what is the requirements to be visualized by 3D-AFM. We believe that the answer is capability of self-organization. For example, in the case of 3D hydration measurements, the hydration structure is significantly disturbed during the vertical tip scan yet it is quickly recovered before starting the next vertical scan. Such a self-organization capability is essential for visualizing inside of 3D structures. One may think this is too severe condition yet we can find large number of important 3D self-organizing systems in both natural and artificial environments. Examples include interfacial phenomena and devices (hydration, lubrication, electric double layer devices and liquid crystal devices) to biological systems (cells, nucleus, chromosomes and proteins). 3D-AFM may allow us to directly visualize inside of these various 3D self-organizing systems.

Based on this idea, we have recently started to explore inside of various 3D self-organizing systems: polymer-water interfaces, ionic liquid - electrode interfaces, and inside of chromosomes and live cells. With these examples, here I would like to propose to apply 3D-AFM not only for visualizing hydration structures but also for imaging inside of various 3D self-organizing systems.

**NS-Invited On Demand-19 Tackling Instabilities in Hybrid Perovskites from the Macro- to the Nanoscale, Marina Leite**, University of California at Davis **INVITED**

Halide perovskites for optoelectronics are often composed by micro- and nano-scale inhomogeneous constructs. Therefore, high spatial resolution characterization methods are required for mapping and quantifying their electrical behavior. In this talk I will present our latest developments on atomic force microscopy (AFM) methods to assess the dynamic physical and chemical processes that take place in perovskite materials and photovoltaic devices are exposed to light. Briefly, we realize a 4D imaging

method that enables mapping open-circuit voltage (Voc) changes with in real-time (16 seconds per scan), and at the nanoscale (< 50 nm in spatial resolution) based on illuminated Kelvin probe force microscopy (KPFM). Using this paradigm, we have demonstrated ion motion within a single nanoscale grain in MAPbI<sub>3</sub> solar cells upon 1-sun illumination, which results in a residual Voc that lasts for several minutes even under dark conditions. For multi-cation structures, we found that Cs-based perovskites deliver fully reversible and stable nanoscale voltage response, in excellent agreement with macroscopic measurements. We correlate the Voc nanoscale maps with chemical imaging through nano-IR and discover that the local variations in voltage are related to the power conversion efficiency enhancement in KI-treated perovskite. The heterogeneity revealed in both the local electrical and chemical responses reveals that the KI additive migrates out of the perovskite films, yet surprisingly; does not affect device performance. Our functional imaging platform can be extended to other perovskite materials, including Pb-free options. At the macroscopic scale, we provide a detailed comparison between MAPbBr<sub>3</sub> and MAPbI<sub>3</sub> through time-dependent voltage measurements. They reveal that, upon illumination, high-energy photons leads to a > 10x slower voltage decline toward equilibrium than low-energy photons in MAPbBr<sub>3</sub>. Yet, MAPbI<sub>3</sub> shows wavelength-independent decay rate, resulting from ion migration. Through in situ photoluminescence (PL) under environmentally controlled conditions, we resolve a humidity-induced PL hysteresis. Further, we apply a machine learning algorithm to predict the luminescence response for > 12 hs. Concerning the unique behavior of multi-cation perovskites, a correlative microscopy approach is realized, combined with environmental-controlled PL measurements.

**NS-Invited On Demand-31 Programming Assembly of 3D Nanoscale Systems, Oleg Gang**, Columbia University **INVITED**

The ability to organize nano-components into the desired architectures with targeted properties can enable a broad range of nanotechnological applications, from energy materials to information processing. However, we are currently lacking an adaptable and broadly applicable methodology for the bottom-up fabrication of desired nanoscale structures. I will discuss our efforts on establishing a versatile assembly platform based on the molecular programming for guiding the formation of targeted architectures from nano-components of different types. The recent advances on assembly of targeted 2D and 3D periodic organizations, hierarchical structures, and arbitrary designed architectures from DNA-encoded abiotic and biological nano-components will be presented. Finally, I will discuss how these assembly approaches can be used for fabrication of nanomaterials with novel optical, mechanical, and catalytic functions.

**NS-Invited On Demand-37 Nanoelectronic Devices and Architectures for Energy-Efficient Computing, An Chen**, IBM Almaden Research Center **INVITED**

As the CMOS scaling driven by the Moore's Law approaching some fundamental limits, high power consumption and heat dissipation on chip have been recognized as the most critical challenges. The semiconductor industry has explored numerous nanoelectronic devices with the potential to achieve significantly lower power based on unconventional mechanisms, materials, and structures, including steep-slope transistors, phase-transition switches, spintronics, van der Waals devices, etc. For example, the Nanoelectronics Research Initiative (NRI) was funded by the Semiconductor Research Corporation (SRC) for over a decade to pursue the "next switch" beyond CMOS. Despite abundant scientific breakthroughs achieved in these device researches, no beyond-CMOS device has been demonstrated to significantly outperform CMOS for Boolean logic and von Neumann architectures. On the other hand, many nanoelectronic devices have shown unique characteristics, e.g., device-level reconfigurability, built-in memory-in-logic capability, tunable analog behaviors, programmable randomness, etc. They can be utilized in novel architectures and computing paradigms, including reconfigurable logic, analog and neuromorphic computing, compute-in-memory, nonvolatile logic, stochastic computing, etc.

To effectively utilize these unique characteristics in novel architectures, it is essential to cooptimize devices and architectures in order to achieve improved functionalities and efficiency. Both bottom-up (optimizing devices to meet architectural requirements) and top-down (designing circuit blocks and architectures to exploit device properties) approaches are needed. Sustainable and scalable technology advancement is often driven by material and device innovations; therefore, it is important to explore emerging materials and devices capable of native implementations of some novel computing paradigms. At the same time, CMOS technology has also been adopted in many novel computing paradigms, which

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presents not only a mature baseline for comparison but also a formidable competitor. Nanoelectronic devices and architectures need to provide convincing advantages in performance and efficiency over CMOS to justify significant research investment, which should be addressed by comprehensive benchmarking. A holistic approach from material exploration to device engineering and further up to architecture co-design has been emphasized in several research programs, including E2CDA (Energy-Efficient Computing from Devices to Architectures) at NSF, nCORE (nanoelectronic Computing Research) at SRC, etc. This presentation will discuss the opportunities and challenges of nanoelectronic devices and architectures for energy-efficient computing in the context of these recent research programs.

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