

## Materials and Processes for Quantum Computing Focus Topic

### Room 203A - Session MP+EM+MN+NS-MoM

#### Systems and Devices for Quantum Computing I

**Moderator:** Vivekananda Adiga, IBM, T.J. Watson Research Center

9:00am **MP+EM+MN+NS-MoM3 Quantum Supremacy: Checking a Quantum Computer with a Classical Supercomputer, John Martinis, Google Inc** **INVITED**

As microelectronics technology nears the end of exponential growth over time, known as Moore's law, there is a renewed interest in new computing paradigms such as quantum computing. A key step in the roadmap to build a scientifically or commercially useful quantum computer will be to demonstrate its exponentially growing computing power. I will explain how a 7 by 7 array of superconducting qubits with nearest-neighbor coupling, and with programmable single- and two-qubit gate with errors of about 0.2%, can execute a modest depth quantum computation that fully entangles the 49 qubits. Sampling of the resulting output can be checked against a classical simulation to demonstrate proper operation of the quantum computer and compare its system error rate with predictions. With a computation space of  $2^{49} = 5 \times 10^{14}$  states, the quantum computation can only be checked using the biggest supercomputers. I will show experimental data towards this demonstration from a 9 qubit adjustable-coupler "gmon" device, which implements the basic sampling algorithm of quantum supremacy for a computational (Hilbert) space of about 500. We have begun testing of the quantum supremacy chip.

9:40am **MP+EM+MN+NS-MoM5 Active Protection of a Superconducting Qubit against Josephson Amplifier Backaction, Baleegh Abdo, N.T. Bronn, O. Jinka, S.B. Olivadese, A. Corcoles, M. Brink, IBM T. J. Watson Research Center; R. Lake, D.P. Pappas, National Institute of Standards and Technology; J.M. Chow, IBM T. J. Watson Research Center**

Nonreciprocal microwave devices, e.g., isolators and circulators, are key components in high-fidelity, quantum-nondemolition (QND), measurement schemes. They separate input from output and protect the quantum systems from unwanted backaction originated by the output chain. However, state-of-the-art, cryogenic circulators and isolators are disadvantageous in scalable architectures because they are lossy, bulky and use magnetic materials and strong magnetic fields, which are not compatible with superconducting circuits. In this work, we realize and characterize nonreciprocal, superconducting devices suitable for qubit readout, which are formed by coupling two nondegenerate Josephson mixers in interferometric schemes. Nonreciprocity is generated by applying a phase gradient between the same-frequency pumps feeding the devices, which play the role of the magnetic field in a Faraday medium. We incorporate these Josephson-based, nonreciprocal devices into a qubit setup and demonstrate fast, high-fidelity, QND measurements of the qubit while actively protecting it against Josephson amplifier backaction.

10:00am **MP+EM+MN+NS-MoM6 Nonlinear Light-matter Interaction: From Superconducting Qubits to Spins in Diamond, Eyal Buks, Israel Institute of Technology, Israel**

Cavity quantum electrodynamics (CQED) is the study of the interaction between matter and photons confined in a cavity. In the Jaynes-Cummings model the matter is described using the two-level approximation, and only a single cavity mode is taken into account. The interaction has a relatively large effect when the ratio  $E/\hbar\omega$  between the energy gap  $E$  separating the two levels and the cavity mode photon energy  $\hbar\omega$  is tuned close to unity.

The talk is devoted to the study of the light-matter interaction in the nonlinear regime using three different CQED systems. In the first experiment a Josephson flux qubit serves as a two-level system and a superconducting resonator as the cavity [1]. We experimentally find that the cavity response exhibits higher order resonances (called superharmonic resonances) in the nonlinear regime when the ratio  $E/\hbar\omega$  is tuned close to an integer value larger than unity. In the second experiment the interaction between a spin ensemble of diphenylpicrylhydrazyl (DPPH) molecules and a superconducting resonator is explored in the region where  $E/\hbar\omega \gg 1$  [2]. We find that the cavity response is significantly modified when the spins are intensively driven close to their Larmor frequency. Retardation in the response of the spin ensemble gives rise to effects such as cavity mode cooling and heating. In the third experiment the interaction between localized spins in diamond (nitrogen-vacancy and nitrogen substitutional

and a superconducting resonator is studied [3]. We find that nonlinearity imposes a fundamental limit upon sensitivity of CQED-based spin detection.

#### References

1. Eyal Buks, Chunqing Deng, Jean-Luc F.X. Orgazzi, Martin Otto and Adrian Lupascu, Phys. Rev. A 94, 033807 (2016).
2. Hui Wang, Sergei Masis, Roei Levi, Oleg Shtempler and Eyal Buks, Phys. Rev. A 95, 053853 (2017).
3. Nir Alfasi, Sergei Masis, Roni Winik, Demitry Farfurnik, Oleg Shtempler, Nir Bar-Gill and Eyal Buks, arXiv:1711.07760.

10:40am **MP+EM+MN+NS-MoM8 Variations in Surface Dipole-Moment Density with Coverage for C/Au(110) – (2 × 1) and Electroplated Au Ion-trap Electrodes, Dustin Hite, K.S. McKay, National Institute of Standards and Technology (NIST); H.Z. Jooya, ITAMP, Harvard-Smithsonian Center for Astrophysics; E. Kim, University of Nevada, Las Vegas; P.F. Weck, Sandia National Laboratories; H.R. Sadeghpour, ITAMP, Harvard-Smithsonian Center for Astrophysics; D.P. Pappas, National Institute of Standards and Technology (NIST)**

Ion traps, designed to test the feasibility of scalable quantum information processing, suffer from excessive electric-field noise that increases strongly as the ion-electrode spacing decreases in progressively smaller traps. This noise couples to the charge of the ions in the trap causing motional heating, which can result in the decoherence of quantum logic gates. This heating can be reduced by orders of magnitude with the use of cryogenic trap electrodes or by in-situ surface cleaning with ion bombardment in traps with room-temperature electrodes. Many experiments over the past two decades have supported theories that model this noise source as being caused by fluctuations in the dipole moments of contaminant adsorbates on the metallic trap electrode surfaces. Gold electrodes are often used to avoid oxidation and other contaminants, nevertheless a thin carbonaceous layer of approximately 3 monolayers (ML) develops on Au, even due to air exposure alone. In this work, we have studied the model system of C/Au(110) – (2 × 1) to understand the mechanisms for the variations in the surface dipole-moment density as a function of the degree of carbon coverage. We have implemented Kelvin probe force microscopy, along with x-ray photoelectron spectroscopy, to determine an average dipole-moment density with increasing carbon coverage, and have compared the results to density functional theory aided by ab-initio molecular dynamics techniques. We find a nearly linear decrease in the work function with a rate of approximately -0.7 eV/ML for sub-monolayer coverages, a regime in which trapped ions have been observed to have a maximum rate of heating. Finally, we compare the results for the model system to those for a microfabricated ion-trap chip with electroplated Au electrodes contaminated with a native hydrocarbon layer incrementally removed by ion bombardment.

11:00am **MP+EM+MN+NS-MoM9 A Compact Cryogenic Setup for Quantum Computing with Trapped Atomic Ions, Ismail Inlek, R. Spivey, G. Vrijsen, Z. Jia, J. Kim, Duke University**

Trapped atomic ions are standard qubits for quantum computing with their long coherence times and high-fidelity qubit operations for universal quantum logic gates. However, conventional trapped ion systems often utilize bulky vacuum and optics setups, hindering scalability and ease of use. We aim to address these infrastructure issues by packaging micro-fabricated ion traps in an ultra-high vacuum (UHV) environment and designing optics to be an integral part of the overall system. Additionally, small footprint of the sealed UHV package allows users to easily install it on a cryostat to benefit from lower heating rates and further reduced vacuum levels. Moreover, these ion trap packages can be conveniently swapped to benefit from micro-fabricated ion trap manufacturing improvements without external UHV maintenance requirements. Towards achieving this goal, we report successful ion trapping in a compact cryogenic setup and characterize the performance of our apparatus for quantum computing applications.

11:20am **MP+EM+MN+NS-MoM10 Advances in Trapped Ion Quantum Computing, Jungsang Kim, Duke University** **INVITED**

Trapped ions provide a highly desirable physical substrate on which to construct a scalable quantum computer. All qubits are exactly identical by nature, can be well isolated from the environment to establish long coherence times, and high fidelity quantum logic gates have been readily available. Furthermore, the long-range Coulomb interactions used for multi-qubit gates in a chain allows for highly connected network of qubits that are fully programmable, opening up opportunities for advanced and

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flexible quantum computer architectures. Some of the most advanced and complex quantum algorithms have been implemented in trapped ion systems leveraging these features. On the other hand, the ion trap systems so far have mainly relied upon conventional methodology used in atomic physics labs to set up the lasers, vacuum chambers and their optical alignments to realize the system. Novel integration technologies, including micro-fabrication, micro-electromechanical system (MEMS), and advanced packaging approaches have been adopted in the past decade to push the integration level for trapped ion systems. In this presentation, I will summarize the state-of-the-art systems used to implement quantum computing applications in the laboratories today, and also outline system design approach currently undertaken to improve the stability, reliability, and programmability of trapped ion quantum computers. Then, I will discuss the opportunities and challenges ahead for reaching a scalable quantum computer capable of executing useful tasks.

## Nanometer-scale Science and Technology Division

Room 102B - Session NS+2D+AN+EM+MN+MP+PC+RM-MoM

### IoT Session: Nanostructured Devices and Sensors

Moderators: David Czaplewski, Argonne National Laboratory, Liya Yu, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM1 Integrating Nanodiamonds with Augmented Artificial Intelligence and Digital Health to Optimize Combination Therapy, Dean Ho, UCLA** INVITED  
Dean Ho, Ph.D.

Nanodiamonds have emerged as promising candidates for clinical drug delivery due to their ability to carry a wide range of candidate therapies, unique surface properties, and biological tolerability. This lecture will highlight our recent clinical trial to validate a nanodiamond-embedded biomaterial for root canal therapy indications [1]. We will discuss the broad spectrum of efficacy, safety, characterization, and other studies that bridged in vitro with preclinical and downstream in-human studies. This lecture will also discuss upcoming clinical nanodiamond-based drug carrier studies, as well as our work in augmented artificial intelligence (AI) to develop globally optimized nanodiamond-modified therapy. Pairing nanodiamond platforms with augmented AI will lead to major advances in drug development and markedly improve response rates and treatment outcomes for a broad spectrum of disorders. Our recent clinical trials using these powerful combination therapy optimization technologies and digital health platforms to scale their implementation to usher in a new era of nanomedicine-based treatment will also be discussed [2].

1. Lee et al., Proceedings of the National Academy of Sciences, 2017
2. Zarrinpar et al., Science Translational Medicine, 2016

9:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM3 Morphology-Controlled Large-Scale Tin Oxide Nanostructures for Highly Sensitive Room Temperature Gas Sensor, Amrit Sharma, Norfolk State University**

Highly sensitive large-scale tin oxide ( $\text{SnO}_2$ ) nanostructures were grown on a glass substrate by vapor-liquid-solid (VLS) process using a mixture of anhydrous tin (II) chloride ( $\text{SnCl}_2$ ) and zinc chloride ( $\text{ZnCl}_2$ ) powders. We demonstrate a new kind of single cell vapor deposition system to precisely control nanostructural morphology by changing the weight ratio of  $\text{SnCl}_2$  and  $\text{ZnCl}_2$  and growth temperature. The morphology and structural property of as-grown nanostructures were characterized using scanning electron microscopy (SEM) and X-ray diffraction (XRD). The SEM images revealed that the  $\text{SnO}_2$  nanostructures with different densities, sizes, and shapes can be achieved by adjusting the weight ratio of  $\text{SnCl}_2$  and  $\text{ZnCl}_2$ .  $\text{SnO}_2$  nanostructures with diameter  $\sim 20$  nm and length  $\sim 100$  nm showed  $\sim 85\%$  sensitivity and 53 seconds of response time, whereas the nanorods with diameter  $\sim 100$  nm and length  $\sim 1$   $\mu\text{m}$  showed  $\sim 50\%$  sensitivity with 198 seconds response time. The nanostructured material with small size and shape showed better sensitivity on sensing at room temperature compared to previously reported  $\text{SnO}_2$  based sensors.

9:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM4 Improving the Localized Surface Plasmonic Resonance Sensing Properties by Composite Metal/Dielectric Mixtures, Steven Larson<sup>1</sup>, Y. Zhao, University of Georgia**  
Localized surface plasmon resonance (LSPR)-based sensors, whose resonance absorbance wavelength responds to the change in the local

dielectric environment have attracted great attention and have been widely studied over the past decade. These sensors are traditionally improved by modifying the shape, size, and gap in the plasmonic nanostructure of the sensor. The sensitivity can also be tuned by the dielectric constant of the plasmonic material, such as noble metal alloys, but the improvements are not significant. Here we show that using a metal-dielectric composite, one can significantly improve the sensitivity of a LSPR sensor. Regular nanotriangle pattern samples composed of a mixture of Ag and  $\text{MgF}_2$  with different composition ratios are prepared by combining nanosphere lithography and electron beam co-deposition. The plasmon resonance of these composite nanostructures at high Ag composition ( $C_{\text{Ag}}$ ) are shown to redshift with  $C_{\text{Ag}}$  until a composition threshold ( $C_{\text{Ag}} \leq 90\%$ ) is met, where the resonance wavelength is nearly constant, slightly blue shifting. Multiple morphological and compositional characterization techniques are used to confirm that the shifts in the plasmonic properties are due to the change in composition and not a change in the morphology. The resulting LSPR sensor at  $C_{\text{Ag}} = 90\%$  can achieve a sensitivity of 696 RIU/nm, as compared to 312 RIU/nm for the same nanotriangle with pure Ag. This significantly improved sensitivity is due to the modified dispersion relationship of the dielectric constant by the composite and will play an important role in future plasmonic material design and applications.

9:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM5 Improving the Selectivity of Tin (IV) Oxide Paper Based Gas Sensors with Plasma Surface Modification, Kimberly Hiyoto, E.R. Fisher, Colorado State University**

Metal oxide nanomaterials are desirable for solid-state gas sensors because of their ability to detect a wide variety of gases through changes in resistance resulting from gas-surface interactions. When optimizing these sensors, the supporting substrate is rarely considered, resulting in devices that are often brittle and have a fixed amount of nanomaterial that can be exposed to target analytes. Recent work using paper as the supporting substrate yields more affordable sensors that are flexible, allowing for a more robust device. Furthermore, the porous morphology of the paper also provides a larger surface area to attach metal oxides when compared to a traditional flat substrate of the same dimensions. Another limitation of these metal oxide sensors is inherent in the detection method. The lack of selectivity and required operating temperature of  $\geq 300$  °C limits the widespread use of metal oxide sensors. Dopants or the addition of a filter in the device design are typical approaches to address these problems; however, this increases fabrication complexity and cost. Plasma processing is a promising strategy to address these issues because it maintains desirable bulk properties but modifies the surface of the material to enhance gas sensor performance.

Here, we describe the  $\text{Ar}/\text{O}_2$  plasma modification of paper based, tin (IV) oxide ( $\text{SnO}_2$ ) nanoparticle devices as a function of applied rf power and precursor pressure. After plasma modification, the paper-based sensors exhibited improved response to carbon dioxide, ethanol, and benzene when compared to the untreated material on a more traditional substrate, zirconium dioxide. Additionally, sensor response to a target gas changed depending on the plasma modification parameters used, indicating the selectivity of these  $\text{SnO}_2$  sensors can be easily tailored via plasma processing. Response and recovery studies of both the treated and untreated sensors will be discussed to demonstrate the dynamic behavior of these devices to the target gases as another measure of gas sensor performance and durability. Along with sensing behavior, optical emission spectroscopy and X-ray photoelectron spectroscopy provide insight into how the plasma modified the material, ultimately elucidating the relationship between material surface chemistry and sensor selectivity. Finally, preliminary work using this same fabrication process with another type of metal oxide gas sensor will be discussed to demonstrate the applicability of this method for other types of materials. Ultimately, these data work toward improved understanding of the gas sensing mechanism to design better performing gas sensors.

10:00am **NS+2D+AN+EM+MN+MP+PC+RM-MoM6  $\text{TiN}@\text{Si}_3\text{N}_4$  Core-shell Heterostructures as Nanoantennas for Photocatalytic Reforming of Methanol, Alejandro Alvarez Barragan, L. Mangolini, University of California, Riverside**

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of nanoantennas for photocatalysis. Aluminum, gold, and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into chemically active catalysts —such as platinum and palladium— adsorbed to their surface. However, the low response of aluminum at visible-near

<sup>1</sup> NSTD Student Award Finalist

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infrared (vis-NIR) wavelengths, the high cost of silver and gold, and the low thermal stability of these three metals, inspire the quest for alternative plasmonic materials that could potentially expand the field towards more ambitious and cost-effective applications. Titanium nitride (TiN) is a conductive ceramic with high hardness and bulk melting point (2930 °C). Its plasmon resonance located in the vis-NIR region, low cost relative to gold and silver, and well-understood properties as a thin film in the semiconductor industry, make it a strong alternative to mainstream plasmonic metals. The present work encompasses a comprehensive study of the oxidation kinetics of TiN particles at the nanoscale and an exploration of its role as nanoantennas for light-induced methanol reformation. TiN particles are synthesized via a scalable, modular, non-thermal plasma method. Titanium and nitrogen precursors are transported into a RF frequency plasma where TiN particles nucleate and grow. The high surface area and nitrogen deficiency of the particles facilitate the oxidation of the material and weaken its plasmonic response. The introduction of a secondary reactor with an input of SiH<sub>4</sub> as precursor gas leads to the formation of a Si<sub>3</sub>N<sub>4</sub> coating. STEM and XPS analyses show that Si<sub>3</sub>N<sub>4</sub> acts as a diffusion barrier, dramatically reducing the oxidation of the ~8 nm TiN particles. UV-vis-NIR spectrophotometry data show that the core-shell heterostructures experience a substantial blue-shift of the plasmon peak and an increase in intensity compared to the bare TiN. Platinum nanoparticles were subsequently deposited on the TiN@Si<sub>3</sub>N<sub>4</sub> by photo-induced reduction of an aqueous solution of chloroplatinic acid. After rinsing and centrifuging, the Pt/TiN@Si<sub>3</sub>N<sub>4</sub> heterostructures were diluted in a 50:50 water/methanol solution. Upon photoexcitation via white light illumination, hydrogen generation was readily detected by gas chromatography. This work also highlights the wide range of applications available for light-induced processes, ranging from materials processing (deposition of Pt particles) to photocatalysis (methanol reforming). It also strengthens the case for alternative plasmonic materials in a field dominated by precious metals.

10:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM8 Nanostructured Sensor and Device Applications of Infiltrated Zinc Oxide**, *Leonidas Ocola*, Argonne National Laboratory; *Y. Wang, J. Chen*, University of Wisconsin-Milwaukee; *P. Blaisdell-Pijuan*, California State University-Fullerton; *R. Divan*, Argonne National Laboratory

**INVITED**

With the increased portfolio of materials deposited using atomic layer deposition (ALD) there has been an increased interest in infiltrated metal oxides such as zinc oxide for novel applications. We find that ZnO metal oxide ALD infiltration can be useful for nanoscale resolution imaging of biological samples and to fabricate novel UV and gas nanosensors with high sensitivity. The ALD infiltration utilizes similar concepts of the ALD coating process with the significant difference in process exposure times, pressure, and purpose. The purpose is to allow the precursor gases infiltrate a porous media (such as a dry biological sample or a photoresist polymer) and allow the reaction to occur inside the material matrix.

In terms of device fabrication we use SU8 as a negative resist that allows for localization of the infiltration process. We have used this property to make a device that is UV sensitive, and that is sensitive to ppm concentrations of gases by using infiltrated zinc oxide. The large bandgap and semiconductor properties of ZnO allow for a visible-blind ultra violet light sensor. We used a standard UV flashlight that emits at 408 nm as the UV source. We also tested the same device for sensing gases like nitrous oxide and formaldehyde. We show that the device can detect these gases with concentrations of 5 ppm. The change in current for such low concentrations was measured to be between 25% and 35%.

With the purpose of investigating quantum applications of infiltrated ZnO, we also have characterized the growth of ZnO in PS-b-PMMA block copolymers (BCP) of spherical and cylindrical sub-20 nm morphologies and studied how the photoluminescence of these nanostructures varies per its seed layer. We report blue-shifted photoemission at 335nm (3.70eV), suggesting quantum confinement effects. Samples of ZnO prepared with an alumina seed layer showed additional defect state photoemission at 470nm and 520nm for spherical and cylindrical BCP morphologies, respectively. Defect photoemission was not observed in samples prepared without a seed layer. No Raman peaks were observed for any samples with less than four cycles of ZnO, implying the absence of phonons and the functionality of these ZnO nanostructures as isolated emitters. To that effect we have demonstrated a fabrication path to isolate single infiltrated cylinders, paving the way for further studies of optical properties of individual 20 nm ZnO nanostructures.

- Use of the Center for Nanoscale Materials an Office of Science user facility, was supported by the U.S. Department of Energy, Office of Science, Office of Basic Energy Sciences, under Contract No. DE-AC02-06CH11357.

11:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM10 Templates for the Investigation of Size-Selected Nanocluster Networks**, *Patrick Edwards*, *V.V. Kresin*, University of Southern California

The study of metal nanoclusters has revealed quantum nanoscale effects unique to the fully size-resolved regime. A highly notable example is electronic shell structure, akin to that in atoms and nuclei, which arises when confined conduction electrons organize into discrete energy levels. One consequence is the possibility of dramatic enhancement in electron Cooper pairing. Recent research from our group has provided evidence of this enhancement in certain free Al nanoclusters, with the electronic transition taking place at a temperature two orders of magnitude above that of bulk aluminum. We now aim to take advantage of this phenomenon by exploring the pairing transition in size-selected nanoclusters soft-landed on an appropriate substrate. Of particular interest are graphene and nanotube device architectures which provide unique templates for organizing nanocluster arrays. For example, a network of such superconducting nanoislands may induce superconductivity in graphene even at low coverages. Theory also predicts that an array of nanoclusters will not only support, but even enhance the Josephson current by 2-3 orders of magnitude. Carbon allotropes offer two distinct advantages for our system. First, the weak out-of-plane bonding provides a surface with less potential to disturb the structure of the soft-landed nanoclusters. Second, the tunability of graphene and carbon nanotube-based field effect transistors offers a versatile probe of nanocluster properties. We are also investigating the use of biological nanowires (bacterial flagella) as potential scaffolds upon which to deposit such nanocluster networks. These abundant and naturally occurring nanowires could serve as low cost and highly reproducible alternatives to the more common metallic or semiconductor templates.

Research supported by the Army Research Office (W911NF-17-1-0154).

11:40am **NS+2D+AN+EM+MN+MP+PC+RM-MoM11 High Performance Detection for X-ray and g -ray with MAPbX<sub>3</sub> Perovskite Single Crystals**, *X. Wang, Z. Zhu, Q. Li, J. Wu, X. Zhang, B. Wang, Wei Lei*, Southeast University

Recently, organometallic lead trihalide perovskites have emerged as a new generation of opto-electronic materials. However, the high performance detection for x-ray and gamma-ray with MAPbX<sub>3</sub> is still a big challenge. For x-ray and gamma-ray detections, the detectors should have high sensitivity. If the photon counting method is adopted, the high energy resolution and high time resolution are also required. In this work, the large area MAPbBr<sub>3</sub> single crystal has been fabricated with a facile methodology. Due to the quite thick active material and large carrier mobility, the x-ray photons and gamma-ray photons can be absorbed with high efficiency. The photo generated electrons and holes can also be collected effectively with the large electric field. To decrease the dark current in the detection, a novel photo-diode structure is proposed here. In crystallization process of MAPbI<sub>3</sub> single crystal, the p-n junction can be formed with doping of selenium atoms into MAPbI<sub>3</sub> single crystal.

With various temperature method, the 30mm×30mm×7mm MAPbBr<sub>3</sub> single perovskite crystal is fabricated. As the experimental results shown, almost all of the 100 keV x-ray photons are absorbed when the MAPbBr<sub>3</sub> SPC is 7mm thick. The detection sensitivity is as high as 305 μC Gy<sub>air</sub><sup>-1</sup>cm<sup>-2</sup> when the anode voltage of x-ray tube is 30 kV .

To reduce the dark current in the detection, two type of photo diode structures have been proposed here. Firstly, a photo diode with structure of Au/TPD/MAPbBr<sub>3</sub> PSC/C<sub>60</sub>/PCBM/Ag has been fabricated with spin coating and sputtering methods. Although the dark current density can be reduced to 20 nA/cm<sup>2</sup> with -30V bias voltage, the temporal response time is nearly 50 μs due to the defects on the interfaces between PSC and carriers transport layers. Then, by doping selenium (Se) in MAPbI<sub>3</sub> perovskite single crystals (DPC) crystallization process, low dark current p-n junctions were fabricated without any organic layers. This photodiodes gives the high detection sensitivity as 21000 mC Gy<sub>air</sub><sup>-1</sup>cm<sup>-2</sup> and 41 mC Gy<sub>air</sub><sup>-1</sup>cm<sup>-2</sup> for 60 keV x-ray and 1.33 MeV gamma-ray respectively. In this photodiode, the transition time becomes shorter under higher electric field, and the carrier lifetime also becomes shorter due to the dopant of Se atoms. Finally, the temporal response time is measured as 3 μs by experiments. The FWHM width of energy spectrum is decreased to 3.2%@1330 keV.

## Biomaterial Interfaces Division

### Room 101B - Session BI+AS+IPF+MN-MoA

#### Advanced Imaging and Structure Determination of Biomaterials Research

**Moderators:** Dan Graham, University of Washington, Axel Rosenhahn, Ruhr-University Bochum, Germany

#### 1:20pm BI+AS+IPF+MN-MoA1 NMR Relaxometry as a Medical Diagnostic, *Michael J. Cima*, Massachusetts Institute of Technology **INVITED**

This talk will describe the diagnostic capabilities of magnetic resonance imaging (MRI) when brought to the patient bedside. Rather than imaging, NMR can be used for important chemical/physiologic diagnostic endpoints. Two will be discussed here; quantifying fluid overload and measurement of hypoxia within tumors. Assessment of intra- and extra-vascular volume is integral in managing patients with heart, liver, and kidney disease as volume status is closely linked to mortality. Commonly used determinants of volume status, such as physical exam and ultrasonography, lack sensitivity and specificity and require expertise in clinical practice. This talk reports on nuclear magnetic resonance (NMR) methods to a portable and clinically useful device. A clinical study with hemodialysis patients and age-matched healthy controls was performed at MGH. The T2 relaxation times of study participants' legs were quantified at multiple time points with both a 1.5T clinical MRI scanner and a custom 0.27T single-voxel MR sensor. The results showed that first sign of fluid overload is an increase in the relative fraction of extracellular fluid in the muscle. The relaxation time of the extracellular fluid in the muscle eventually increases after more fluid is accumulated. Importantly, these MR findings occur before signs of edema are detectable on physical exam. Solid tumors are often hypoxic and characterized by an extreme lack of oxygen. Tumor hypoxia imparts significant negative outcomes for patients but is highly variable within cancer types and patient populations. Many of these poor clinical outcomes can be tied to hypoxic-induced radiotherapy resistance. Resistance to radiotherapy in hypoxic regions can be overcome by increasing the dose delivered but exposure limitations of healthy tissue and organs must be considered. The lack of a viable quantitative clinical oxygen measurement method prevents safe dose escalation in these patient populations. Here we report on a silicone-based quantitative oxygen sensor. The MRI contrast of this material depends on dissolved oxygen. Thus, the material functions as a first of its kind solid-state contrast agent. The sensor leverages the existing MRI hardware, which is part of the current clinical work flow, to map tumor oxygen content. This information can then be integrated into the dose planning process clinicians currently conduct to selectively and safely boost dose to low oxygen tumor subvolumes. This sensor is approved by the institutional review board at Dana Farber Cancer Center for a clinical trial in patients locally advanced cervical cancer.

#### 2:00pm BI+AS+IPF+MN-MoA3 Direct Observation of Cell Signaling Proteins Interacting with a Model Cell Membrane by Sum Frequency Generation Vibrational Spectroscopy, *T.W. Golbek*, Oregon State University; *T. Weidner*, Aarhus University, Denmark; *C.P. Johnson*, *Joe Baio*, Oregon State University

Proteins that contain C2 domains are involved in a variety of biological processes including encoding of sound, cell signaling, and cell membrane repair. Of particular importance is the interface activity of the C-terminal C2F domain of otoferlin due to the pathological mutations known to significantly disrupt the protein's lipid membrane interface binding activity, resulting in hearing loss. Therefore, there is a critical need to define the geometry and positions of functionally important sites and structures at the otoferlin-lipid membrane interface. Here we describe the first *in situ* probe of the protein structure of otoferlin's C2F domain interacting with a cell membrane surface. To identify this protein's structure at the lipid interface we applied sum frequency generation (SFG) vibrational spectroscopy and coupled it with simulated SFG spectra to observe and quantify the otoferlin C2F domain interacting with model lipid membranes. A model cell membrane was built with equal amounts of phosphoserine (PS) and phosphocholine (PC). SFG studies that examined the ordering of the lipids that make up the model membrane, demonstrate that lipid fusion occurs after docking of the otoferlin C2F domain via the observation of a 62% increase in amplitude from the SFG signal near 2075  $\text{cm}^{-1}$  assigned to specific groups within the model membrane. This increase is related to lipid ordering caused by the docking interaction of the otoferlin C2F

domain. SFG spectra taken from the amide I region contain peaks near 1621  $\text{cm}^{-1}$  and 1672  $\text{cm}^{-1}$  related to the C2F domains beta-sandwich secondary structure, thus, indicating that the domain binds in a specific orientation. By mapping the simulated SFG spectra to the experimentally collect SFG spectra, we found the C2F domain of otoferlin orients 32° normal to the lipid surface. This information allows us to map what portion of the domain directly interacts with the lipid membrane. Furthermore, we show first experimental view of any C2 domain of otoferlin docked at the membrane interface, thereby, validating SFG as a method to probe C2 domain-membrane interfaces.

#### 2:20pm BI+AS+IPF+MN-MoA4 Vibrational Sum-frequency Scattering Spectroscopy for the Characterization of Protein Fiber Structures and their Surface Interactions in Biological Environments, *Patrik K. Johansson*, *D.G. Castner*, University of Washington

Biological processes are typically regulated by interactions at the interface of 3D structures, such as the membrane of cells or protein fiber surfaces. Collagen (the most common protein in mammals) forms large fibers that are responsible for the structural integrity of tissues. The structure, organization and interactions of these fibers are furthermore important for the survival, communication, migration, and proliferation of cells.

Investigating protein fiber interactions is challenging, particularly under biological conditions where the fibers exist in a 3D aqueous environment. Many techniques cannot interrogate interfaces buried in the bulk of a solvent and therefore require 2D surface models, while others need extensive purification and sample preparation. These approaches may not capture all key characteristics of the fiber surface structure and interactions in the real sample. However, vibrational sum-frequency scattering (SFS) spectroscopy, with inherent contrast for local molecular ordering, can be utilized towards these important goals.

As a first demonstration, we have applied SFS to protein fibers in aqueous environments, self-assembled from collagen type I. We detected signals from the amide I band and the N-H stretching vibrations, both of which are related to the specific protein backbone structure. Signals from the C-H stretching and bending vibrations were also identified, which are more associated with the side-chains in the fibers. The angular scattering patterns for the backbone (amide I) and side-chain (C-H stretches and bends) signals are different, making the spectra dependent on the angle of detection. While the backbone signals are dominant in the phase-matched direction, the side-chain signals remain high also at large scattering angles. Distinctions in the organizational symmetry and the relative fiber surface contribution to the overall signal are hypothesized as reasons for this observation.

Finally, we are investigating the impact of changes to the environment (e.g. ionic strength, pH, surfactants) on the shape of spectra and scattering patterns for the detected SFS signals. This could yield new insights to the structure and dynamics of collagen fibers in biological settings. The relevance of such investigations is enhanced by the fact that detection of vibrations from the surrounding molecules is a direct observation of their interactions with the collagen fiber surface, which thus can be correlated with the fiber structure. The relative orientations for the detected groups can also be obtained via vibrational SFS polarization analysis, for a deeper understanding of biomolecular interactions in biological processes.

#### 2:40pm BI+AS+IPF+MN-MoA5 How Proteins Grow Calcium Carbonates – The Mechanism of Vaterite Bioprecipitation Studied at the Molecular Level by Sum Frequency Generation Spectroscopy, *H. Lu*, Max Planck Institute for Polymer Research, Germany; *S. Roeters*, Aarhus University, Denmark; *H. Lutz*, *M. Hood*, *A. Schäfer*, Max Planck Institute for Polymer Research, Germany; *R. Muñoz-Espí*, Universidad de Valencia, Spain; *M. Bonn*, Max Planck Institute for Polymer Research, Germany; *Tobias Weidner*, Aarhus University, Denmark

Proteins can act as Nature's engineers at interfaces and manipulate hard tissue growths. Specialized peptides can bind and release specific mineral facets and grow the intricate mineral morphologies found in diatom cell walls, mollusk nacre, but also human teeth and bone. Taking clues from Nature we aim at understanding the mineralization processes at the molecular level and to develop design rules for biogenic nanophase materials. Mineral proteins control the biogenesis of  $\text{CaCO}_3$  by selectively triggering the growth of calcite, aragonite or vaterite phases. The templating of  $\text{CaCO}_3$  by proteins must occur predominantly at the protein/ $\text{CaCO}_3$  interface. Surprisingly, molecular-level insights into the interface during active mineralization have been lacking. Here, we investigate the role of peptide folding and structural flexibility on the mineralization of  $\text{CaCO}_3$ . We discuss the mineral activity of amphiphilic

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peptides based on glutamic acid and leucine with  $\beta$ -sheet and  $\alpha$ -helical secondary structures. While both sequences lead to vaterite structures, the  $\beta$ -sheets yield free-standing vaterite nanosheet with superior stability and purity. Surface-specific spectroscopy studies and molecular dynamics simulations reveal that the interaction of calcium ions with the peptide monolayer restructures both the peptide backbone and side chains. This restructuring enables effective templating of vaterite by mimicry of the vaterite (001) crystal plane. The approach is universally applicable to mineral peptide engineering. We will discuss how analogous peptide designs can be used to steer the growth not only of calcium carbonates but also calcium oxalates.

3:00pm **BI+AS+IPF+MN-MoA6 ToF-SIMS Imaging of Chemical Modifications in Topographically Challenging Materials, Michael Taylor, D.J. Graham, L.J. Gamble, University of Washington**

Three-dimensional (3D) porous materials are applied in a variety of areas within materials science<sup>1</sup>. Pores in catalysts provide a high surface reaction area, pores in biofilters facilitate fluid movement for biomolecule capture, and pores in tissue engineered constructs allow for cellular ingress and vascularization. These applications require surface modifications to add specific functionality to their surfaces. The successful functionality of these materials is related to the ability of these modifications to reach all surfaces of the pores. However, it is challenging to characterize these complicated materials and verify the presence and distribution of these surface modifications. Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) is a powerful label-free surface analysis tool that can be used to image the molecular composition of cells, tissues and polymers. Porous 3D materials however, are non-ideal for ToF-SIMS analysis as the technique is highly surface-sensitive, topography on the order of microns can inhibit the ability to produce secondary ions related to surface modifications. To solve this problem we have developed a methodology for filling voids in porous materials to produce a surface where ToF-SIMS imaging may be performed. A embedding process for porous materials with poly(vinyl alcohol)(PVA) is detailed followed by freezing and cryo-sectioning to expose the modified scaffold interior. Here, we demonstrate the versatility of this method by high spatial resolution 3D imaging of a number of surface modifications in PCL poly(caprolactone) scaffolds<sup>2</sup>. Characterisation of fluorocarbon (FC) films deposited using octafluoropropane (C3F8) plasma enhanced chemical vapor deposition (PECVD) will be demonstrated, showing that increased treatment times deposits uniform coatings while shorter treatment results in a gradient distribution of FC throughout the PCL scaffold. Additionally we show data on imaging immobilized/adsorbed proteins within PCL scaffolds. Using this methodology we demonstrate that high spatial resolution label-free 3D imaging of chemical modifications in materials with complex geometries is now possible with ToF-SIMS.

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(2) Taylor, M. J.; Aitchison, H.; Hawker, M. J.; Mann, M. N.; Fisher, E. R.; Graham, D. J.; Gamble, L. J. Time of Flight Secondary Ion Mass Spectrometry—A Method to Evaluate Plasma-Modified Three-Dimensional Scaffold Chemistry. *Biointerphases* **2018**, *13* (3), 03B415 DOI: 10.1116/1.5023005.

3:40pm **BI+AS+IPF+MN-MoA8 Imaging Plant and Plant Growth-Promoting Bacteria Interactions Using Time-of-Flight Secondary Ion Mass Spectrometry, Xiao-Ying Yu, R. Komorek, Z.H. Zhu, C.J. Jansson, Pacific Northwest National Laboratory**

We present the first imaging and spectra results of plant root interactions with plant growth-promoting bacteria (PGPB) using time-of-flight secondary ion mass spectrometry (ToF-SIMS), showing the successful application of delayed image extraction to study plant biology. Compared to MALDI (Matrix Assisted Laser Desorption Ionization), an imaging mass spectrometry technique widely used in plant studies,<sup>[1]</sup> SIMS is less destructive and provides submicrometer spatial mapping of molecular species of importance in metabolic processes. *Brachypodium distachyon* (*Brachypodium*), a genomics model for bioenergy and native grasses, is used due to its small diploid genome, close phylogenetic links to other grass species, relative ease of genetic transformation, short life cycle, small stature, and simple growth requirements.<sup>[2]</sup> Plant growth-promoting bacteria (PGPB) such as *Pseudomonas* and *Arthrobacter* were introduced to *Brachypodium* roots prior to analysis, and their potential effect on root extrusion was studied using ToF-SIMS imaging. Specifically, delayed image extraction was used in data acquisition. This approach was chosen to

obtain high mass and high spatial resolutions.<sup>[3]</sup> Excellent SIMS imaging gives topographical description of the root surface with and without PGPB interactions. Distinctive characteristic peaks are observed, indicating compositional changes with and without PGPB introduction to the root surface beside visible surface morphological variations. Our initial results demonstrate that ToF-SIMS is a promising imaging mass spectrometry tool to study plant biology and root-microbe interactions and provide molecular-level insight at the biointerface with high spatial resolution.

## References:

[1] D Sturtevant *et al.*, Three-dimensional visualization of membrane phospholipid distributions in Arabidopsis thaliana seeds: A spatial perspective of molecular heterogeneity, *Biochimica et Biophysica Acta* (2017), **1862**(2), 268-81.

[2] T Girin *et al.*, Brachypodium: a promising hub between model species and cereals, *J. Experimental Botany* (2014), **65**(19), 5683-96.

[3] QP Vanbellingen *et al.*, Time-of-flight secondary ion mass spectrometry imaging of biological samples with delayed extraction for high mass and high spatial resolutions, *Rapid Comm. Mass Spectrom.* (2015), **29** (13), 1187-95.

4:00pm **BI+AS+IPF+MN-MoA9 Imaging of Cells and Tissues with Helium Ion Microscopy, J.A. Notte, D. Wei, Chuong Huynh, Carl Zeiss Microscopy, LLC**

Both optical and electron microscopy are well established techniques in the life sciences with established protocols for imaging and sample preparation. However the newly developed helium ion microscope has some unique advantages, and is gaining a reputation for providing insightful, easy to interpret images over a wide range of biological samples and bio-materials. This presentation serves as both an introduction to this novel technique and a review of recent results.

Because helium ions do not suffer appreciably from diffraction effects, they can be focused to a sub-nanometer probe, providing nanometer scale image resolution with a depth of focus that is well suited to complex surfaces and structures. As helium ions interact with the sample, they provide an abundance of secondary electrons that convey surface-specific and topographical information. Distinctly different from the conventional (gallium) focused ion beams, helium ions do not significantly damage the sample from the sputtering process. And importantly, helium ion microscopy is not affected by charging artifacts when imaging insulating materials, even glass slides, so there is no need for metal over-coating which would otherwise obscure finer details.

Example images will include a pancreatic cell membrane showing the pores and cilia present on their natural surfaces. Other examples will show the complex structure of the principal cell and intercalated cells of the collecting duct of a rat kidney. Other imaging results from diverse fields include stony corals, collagen networks, bone minerals, stereocilia, otoconia, actin filaments, and cryptococcus neoformans. False colored images of the multi-ciliated epithelial trachea of an adult mouse and T4-phages will also be presented. Finally, new results will be shown from the SIMS spectrometer which provides elemental and isotopic information, and can be the basis for true colorization.

In this talk, an emphasis will be placed on the physics principles that enable these imaging results. The selected examples serve to demonstrate the breadth of results that can be attained with this relatively new technique.

4:20pm **BI+AS+IPF+MN-MoA10 Quantitative Analysis of Electrolites in Microliter-size Blood Drops Congealed via HemaDrop™ using Ion Beam Analysis and SIMNRA, H. Thinakaran, S.R. Narayan, J.M. Day, Nicole Herbots, F.J. Ark, B. Wilkens, M. Mangus, R.J. Culbertson, Arizona State University**

Accurate analysis of microliter blood samples can improve medical testing and forensics. Most critically ill patients suffer from hospital-acquired anemia due to the large volume currently required for blood diagnostic tests: 7 mL per vial.

Prior attempts by Theraso to analyze microliter-sized blood droplets in liquid form exhibit systematic errors greater than 10%, higher than the acceptable medical threshold.

This research investigates the accuracy of Ion Beam Analysis (IBA) performed on microliter-sized blood droplets congealed into Homogenous Thin Solid Films (HTSFs) using HemaDrop™, a new patent-pending technique using hyper-hydrophilic coatings to condense fluids into a uniform solid state with a smooth surface.

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Prior to IBA analysis, the solidification of blood droplets into HTSF's is observed with optical microscopy and compared to conventional Dried Blood Spots (DBS). DBS exhibit phase separation between platelets and serum, with non-uniform, rough surfaces. Conversely, blood droplets solidified on HemaDrop™-coated surfaces are uniform and smooth, with little phase separation.

Next, quantitative compositional analysis using IBA is performed on  $\mu\text{L}$  blood drops solidified on HemaDrop™ coatings and is compared to results on DBS. HTSFs congealed on HemaDrop™-coated surfaces yield well-defined 2 MeV RBS spectra where individual species and electrolytes (C, N, O, Na, K, Ca, Cl, Fe) can be identified, while none can be distinguished on DBS.

The damage curve method [1] extracts elemental composition while accounting for possible IBA damage. Several consecutive spectra are taken on the sample, and RBS yields are interpolated to their original concentrations.

IBA simulations with the software SIMNRA enable comparison between RBS data and simulations, resulting in elemental composition accurate within 1%. Blood electrolyte compositions via SIMNRA are obtained on successive IBA spectra taken on different areas of the thin solid films and on different HTSFs congealed from the same blood. Relative error analysis between different HTSF samples establishes whether reproducibility within 10% can be achieved.

HemaDrop™ reliably creates stable, uniform, thin solid films to measure blood composition from  $\mu\text{L}$ -volume drops based on comparative IBA results and optical observations. Measurements of elemental composition of HTSF of blood samples are accurate and reproducible. HemaDrop allows for analysis in vacuo from  $\mu\text{L}$  of blood, greatly expanding the range of techniques that can be applied to identify elements and molecules (e.g., antibiotics, proteins).

[1] \*Int & US Patent Pending, 2016, 2017

## Industrial Physics Forum

Room 101B - Session IPF+AS+BI+MN-TuM

### Advanced Imaging and Structure Determination of Biomaterials

**Moderators:** David G. Castner, University of Washington, Michael Grunze, Max Planck Institute for Medical Research

8:00am **IPF+AS+BI+MN-TuM1 Chemical Imaging as a Tool to assess Molecular and Morphologic Content in Natural Tissues and Fabricated Models**, R. Bhargava, T. Comi, M. Gryka, Kevin Lee Yeh, University of Illinois at Urbana-Champaign **INVITED**

Chemical imaging, in which molecular content is obtained using spectroscopy and images are formed using microscopy, is an emerging area to characterize cells and tissues. We present here a chemical imaging approach based on mid-infrared spectroscopic imaging that combines the spatial specificity of optical microscopy with the molecular selectivity of vibrational absorption spectroscopy. IR spectroscopic imaging is particularly attractive for the analysis of cells and tissue in that it permits a rapid and simultaneous fingerprinting of inherent biologic content, extraneous materials and metabolic state without the use of labeled probes. Recorded data are related to the structural and functional state of the biological material using computation. We describe the computational strategy and statistical considerations underlying decision-making for this modality. A combination of theory, novel instrumentation and signal processing forms an integrated approach to biochemical analyses. First, we describe attempts to automate histopathology without dyes or human input. Results indicate that a rapid assessment of tissue is possible. Applied to engineered 3D tissue models for breast tumors, we show that the imaging technology is useful in rapidly assessing culture quality and that the model systems can act to inform researchers about the involvement of different cell types in cancer progression. Finally, we integrate imaging observations with those from conventional biological experiments to provide a complete view of cancer progression in these systems.

8:40am **IPF+AS+BI+MN-TuM3 Fluorescence Dynamics and Nonlinear Optical Imaging Methods for Biomedical Applications**, Alba Alfonso Garcia, L. Marcu, University of California at Davis **INVITED**

Generation of quality bioengineered tissue constructs, a main cornerstone for regenerative medicine, require new tools to monitor their maturation processes. Optical imaging, and in particular fluorescence dynamics and nonlinear optical techniques, provides the means for non-destructive, longitudinal, and quantitative evaluation. Using fiber optics and catheterized imaging systems these strategies are implemented with flexible geometries that allow investigations be performed outside of the realm of the microscope and the microscope slide, but instead *in situ*, on bioreactors, culturing wells and chambers, or even *in vivo*. Fluorescence dynamics and nonlinear optical imaging are especially well suited as they rely on intrinsic properties of the biomaterials to generate contrast. Tissue autofluorescence allows spectroscopic evaluation of tissue components, and the analysis of its temporal dynamics leads to functional analysis of tissue status. Additionally, nonlinear light-matter interactions probe vibrational and electronic energy levels that provide enhanced biochemical specificity of tissue constituents. All these approaches are compatible with label-free strategies, avoiding the addition of labeling agents onto already complicated samples. In this presentation, I will overview applications of fluorescence dynamics and nonlinear optical imaging including fluorescence lifetime imaging, two-photon fluorescence or second harmonic generation in tissue engineering. In particular, I will discuss tracking approaches to visualize recellularization processes on bioengineered vascular constructs. I will also characterize tissue composition of carotid arteries along their length based on their autofluorescence lifetime signals, and how this correlate with the structural protein composition of the vessel wall as evaluated by gold-standard biochemical assays. Finally, we will see how these methods are also applied in different fields such as the generation of cartilage-based implants, and the real-time discrimination of healthy versus diseased tissues in the context of cancer diagnostics.

9:20am **IPF+AS+BI+MN-TuM5 Single Molecule Imaging of Receptor Signalling**, Katharina Gaus, University of New South Wales, Australia **INVITED**

Antigen recognition by the T cell receptor (TCR) is a hallmark of the adaptive immune system. When the TCR engages a peptide bound to the

restricting major histocompatibility complex molecule (pMHC), it transmits a signal *via* the associated CD3 complex. How the extracellular antigen recognition event leads to intracellular phosphorylation remains unclear.

We develop single-molecule localization microscopy (SMLM) approaches and novel analysis to determine how spatial organization regulates signal initiation and propagation. For example, we used SMLM data to map the organization of TCR-CD3 complexes into nanoscale clusters and to distinguish between triggered and non-triggered receptor copies. We found that only TCR-CD3 complexes in dense clusters were phosphorylated and associated with downstream signaling proteins, demonstrating that the molecular density within clusters dictates signal initiation. This lead us to propose a model in which antigen recognition is first translated into receptor clustering and then the density of receptor nanoclusters is translated into signaling. This model may explain how T cells can respond to both the affinity and dose of pMHC molecules with a common signal transduction mechanism (Paeon et al. PNAS 2016). We also developed novel FRET sensors to monitor the rate of receptor clustering (Ma et al. Nat Commun 2017) and a sensor that reports membrane charges (Ma et al. Nat Biotech 2017) to understand how biophysical properties of the plasma membrane contribute to TCR signaling.

11:00am **IPF+AS+BI+MN-TuM10 Developing a Google-earth View of Tumour Metabolism through Multiscale Molecular Imaging**, J. Bunch, Rory T. Steven, National Physical Laboratory, UK **INVITED**

Mass spectrometry (MS) is one of the most powerful techniques for chemical analysis and when combined with an imaging modality allows molecular chemistry to be visualised in 2D and 3D, from the nano- to the macroscale, in ambient conditions and in real-time. There are numerous techniques each having different modes of operation including label-free and labelled analyses.

Cancer Research UK has identified that building an understanding of the inter- and intra- heterogeneity of tumours and their evolution over time and in response to therapy will require greater insight into the underlying biology, using *in vivo* and *in vitro* models and integrating biomarkers into both early- and late-phase trials. In 2017 the Grand Challenge programme was launched. Our collaborative action involves NPL, Imperial College London, The Beatson Institute, ICR, Barts Cancer Institute, The Francis Crick Institute, The University of Cambridge and AstraZeneca. Together we will develop a validated pipeline for multi-scale imaging of tumours collected from GEMMs and patients.

By pursuing a multiscale (organ to organelle) and multi-omics approach with a range of mass spectrometry imaging (MSI) techniques (MALDI, DESI, SIMS and ICP MS), we aim to deepen our understanding of the interplay of genes, proteins, metabolites and the role of the immune system in cancer development and growth.

This presentation will review early results and a discussion of the challenges associated with such a large, multi-technique, multi-site, mass spectrometry project.

11:40am **IPF+AS+BI+MN-TuM12 X-ray Diffraction and Coherent Imaging with Nano-focused Radiation: A Multi-scale Approach from Biomolecular Assembly to Cell, Tissue and Organ**, Jan-David Nicolas, T. Salditt, University of Göttingen, Germany **INVITED**

X-rays deeply penetrate matter and thus provide information about the functional (interior) architecture of complex samples, from biological tissues and cells to novel composite materials. However, this potential of hard x-rays in view of penetration power, high spatial resolution, quantitative contrast, and compatibility with environmental conditions has to date not been fully developed, mainly due to significant challenges in x-ray optics. With the advent of highly brilliant radiation, coherent focusing, and lensless diffractive imaging this situation has changed. We show how nano-focused hard x-rays can be used for scanning as well as for full field holographic x-ray imaging of biological samples [1]. The central challenge of inverting the coherent diffraction pattern will be discussed and different reconstruction algorithms will be presented, from holographic techniques [2] toptychography [3,4]. Next, we will present new approaches to treat the massive diffraction data recorded in scanning nano-diffraction experiments of cells and tissues [5].

By scanning the sample through the focused x-ray beam and recording full diffraction patterns in each scan point, structural parameters can be mapped throughout the cell or histological section [6], offering a 'diffraction contrast' by which one can localize also unstained biomolecular assemblies in cells and tissues, and at the same time investigate their structure. As an example, we address the sarcomeric organization in heart

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muscle cells (cardiomyocytes) [7,8], and show how the sarcomere organization evolves and differs between different cell types and maturation states. As a multi-scale approach, we then discuss sarcomeric structure in heart tissue sections, and then finally present phase contrast tomography reconstructions of an entire mouse heart.

- [1] Bartels et al., Phys. Rev. Lett. (2015), 114, 048103
- [2] Krenkel et al., Acta Crystallogr. A (2017), 73, 282-292
- [3] Giewekemeyer et al., PNAS (2010), 107, 529-534
- [4] Wilke et al., Optics Express (2012), 20, 19232-19254
- [5] Nicolas et al., J. Synchrotron Rad. (2017), 24, 1163-1172
- [6] Carboni & Nicolas et al., Biomed. Opt. Express (2017), 8, 4331-4347
- [7] Bernhardt et al., New J. Phys. (2017), 19, 013012
- [8] Nicolas et al., J. Appl. Crystallogr. (2017), 50, 612-620

## Nanometer-scale Science and Technology Division Room 102B - Session NS+AN+EM+MN+MP+RM-TuM

### Nanophotonics, Plasmonics, and Metamaterials

**Moderators:** Alokik Kanwal, NIST Center for Nanoscale Science and Technology, Nikolai Klimov, National Institute of Standards and Technology

8:00am **NS+AN+EM+MN+MP+RM-TuM1 Parametric Nonlinear Interactions in Nanofabricated Silicon-based Photonics, Amy Foster**, Johns Hopkins University

**INVITED**

High optical confinement waveguides on integrated platforms enable nonlinear optical interactions with low power levels. The third-order nonlinear susceptibility, a modification of a material's permittivity due to an applied optical field, exists in all materials, and is an intensity-dependent process leading to third-order parametric effects. Harnessing the high optical intensities enabled by high confinement waveguides allows standard semiconductor materials to become power-efficient parametric nonlinear optical devices that can operate with powers in the mW range. The optical confinement of a waveguide also enables control over the waveguide's dispersion, allowing for phase-matching of the parametric processes thereby improving its operating bandwidth. Using standard nanofabrication techniques, integrated photonic devices can be tailored in both geometry at the nanoscale, and in magnitude of their third-order susceptibility through modification of their material properties. In this talk, we will discuss a variety of parametric nonlinear optical demonstrations in silicon-based waveguides including optical parametric amplification and oscillation, phase-sensitive amplification, and frequency conversion and comb generation. Furthermore, we will discuss these devices for a variety of applications including optical signal processing, spectroscopy, and security.

8:40am **NS+AN+EM+MN+MP+RM-TuM3 Ultrafast Optical Pulse Shaping using Dielectric Metasurfaces, Amit Agrawal, S. Divitt, W. Zhu, C. Zhang, H.J. Lezec**, NIST Center for Nanoscale Science and Technology

**INVITED**

Since the invention of femtosecond pulsed lasers, the field of ultrafast optical science and technology has seen significant progress in the generation and characterization of ultrashort optical pulses. Complimentary to development in generation and characterization techniques, arbitrary temporal shaping of optical pulses has become an integral part of the field. Fourier-transform pulse shaping is the most widely adopted approach that entails parallel modulation of spatially separated frequency components to achieve the desired pulse shape. Recently, dielectric metasurfaces have emerged as a powerful technology for arbitrary control over the amplitude, phase, or polarization of light in a single, compact optical element. Here, we experimentally demonstrate shaping of sub-10 fsec ultrafast optical pulses using a centimeter-scale silicon metasurface acting as both amplitude and phase modulation mask. The deep-subwavelength silicon nanostructures, positioned with nanometer precision, are individual optimized to provide accurate amplitude and phase modulations to each frequency component. Masks of this type offer a lower cost, larger size, higher resolution, high diffraction efficiency, high damage threshold method for controlling ultrafast pulses.

9:20am **NS+AN+EM+MN+MP+RM-TuM5 Single-Particle Nanophotonics and Materials Investigations with Optical Microresonator Spectrometers, Erik Horal**, University of Wisconsin - Madison; *K.D. Heylman, K.A. Knapper, M.T. Rea, F. Pan, L.T. Hogan, R.H. Goldsmith*, University of Wisconsin-Madison

**INVITED**

Optical microresonators have achieved impressive sensitivities in a range of experimental modalities. We leverage the exquisite sensitivity of microresonators to enable highly sensitive spectroscopic characterization of objects on the surface of the resonator. In this way, not only can single particles be detected and identified, but fundamental properties of interrogated systems can be studied, opening a path to mechanistic studies and label-free chemical identification.

Our photothermal-based technique employs a two-beam geometry. A fiber-coupled (probe) beam records the whispering-gallery mode (WGM) resonance wavelength via evanescent coupling through a tapered fiber, while a second free-space (pump) beam heats absorbing particles or molecules on the surface of the microresonator, shifting the WGM resonance. In essence we use the microresonator as a nearfield thermometer to measure dissipated heat upon optical excitation. To circumvent the photothermal background of the popular SiO<sub>2</sub> on Si toroidal resonators, we have developed an all-SiO<sub>2</sub> microtoroidal resonator, unlocking visible wavelengths to interrogation. We further employed a double-modulation technique through simultaneous Pound-Drever-Hall locking of the probe beam and amplitude modulation of the pump beam to reach sub-100 Hz or single attometer resonance shift resolution. This corresponds to signals much smaller than that predicted from a single-molecule, and thus represents an avenue toward single-molecule absorption spectroscopy.

We demonstrate this technique by examining gold nanorods (AuNR), which validate our experimental setup with near-diffraction limited photothermal maps, Lorentzian absorption spectra with stochastic center wavelengths, and single dipole polarization dependences. Further, AuNRs in close proximity to microresonator WGMs display signatures of photonic-plasmonic interactions, a forest of Fano resonances decorating the plasmonic absorption feature. This platform offers a facile methodology to study these complex interactions, with thermal annealing of the AuNRs producing highly controllable tuning of Fano resonances. Applying our platform to conductive polymers (CP), we have begun to understand the fundamental properties that enable the high conductivity from a bottom-up nanoscale perspective. We examine the interplay between homogeneous and heterogeneous broadening, measure the long-range ordering, and determine relative surface orientation of CPs. These examples firmly demonstrate the utility of our platform to go beyond sensing allowing exploration of novel characteristics in complex systems and potentially the observation of chemical and biochemical dynamics.

11:00am **NS+AN+EM+MN+MP+RM-TuM10 Optomechanical Interactions for Metrology and Signal Processing, Karen Grutter**, The Laboratory for Physical Sciences

**INVITED**

Imprinting radio-frequency (RF) signals on optical carriers has a broad range of applications from metrology to communication and has been accomplished in bulk components using a variety of techniques. Achieving this functionality on a chip could broaden the potential application space, but the bulk frequency generation methods do not translate directly to the nanoscale. A number of methods have been proposed for on-chip frequency generation, including various sources of electro-optic modulation, comb generation via material nonlinearities in microresonators, and optomechanical/opto-acoustic interactions. In this talk, we will discuss the features of these sources, with particular focus on optomechanical interactions.

One potential phenomenon enabling opto-acoustic frequency generation is stimulated Brillouin scattering (SBS), which is essentially an interaction between propagating phonons and photons. This effect has been demonstrated in optical fibers, and recent results in on-chip waveguides show promise. One of the challenges with SBS on chip is that gain is dependent on long interaction lengths.

This interaction can be enhanced by moving to a different domain of phonon/photon interaction: cavity optomechanics. In an optomechanical cavity, the characteristics of the generated frequency are dependent on the mechanical eigenmode. We will demonstrate the relationship between mechanical quality factor and phase noise in ring optomechanical oscillators.

The optomechanical interaction can be optimized beyond that of ring resonators by further confining optical and mechanical modes using



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photonic and phononic crystals. We have designed and fabricated  $\text{Si}_3\text{N}_4$  nanobeam optomechanical crystals with  $\sim 4$  GHz mechanical breathing modes. The increased optomechanical coupling of these nanobeams confers high sensitivity to displacement, which could be exploited for various metrology applications, which we will discuss.

Further enhancement of the optomechanical coupling can be achieved by modifying the optomechanical crystal geometry to support an optical slot mode. We have designed and fabricated  $\sim 3$  GHz-frequency slot-mode optomechanical crystals in  $\text{Si}_3\text{N}_4$ . In addition to increasing the optomechanical coupling compared to the single-nanobeam device, this structure has increased versatility, enabling interaction with other stimuli and modalities. We have integrated NEMS actuators with a slot-mode optomechanical crystal, and used these actuators to tune the optical mode and lock it to an external, fixed laser wavelength. This increases the practicality of this device, enabling longer-term measurements and stabler frequency sources.

11:40am **NS+AN+EM+MN+MP+RM-TuM12 Cold-atom based Sensors and Standards**, *Stephen Eckel, D.S. Barker, J.A. Fedchak, N.N. Klimov, E. Norrgard, J. Scherschligt*, National Institute of Standards and Technology

## INVITED

In this talk, I will describe our recent efforts to merge nanophotonics, ultra-high vacuum, and atomic physics together to build a new generation of cold atom sensors and standards. In particular, I will focus on our recent realization of a single-beam system for cooling lithium atoms, an atomic species recently identified as an excellent candidate for a primary vacuum standard. Our system uses a triangular-shaped nanofabricated diffraction grating to produce the necessary beams for a magneto-optical trap that cools and slows the atoms. Unlike systems that use rubidium or cesium, which can be loaded from a vapor, lithium introduces additional complications because it must be produced from a thermal source requiring loading of the magneto-optical trap from behind the chip. Finally, I will conclude by talking about other trap geometries that we are pursuing, how they benefit vacuum and inertial sensors, and what the synergy of integrated nanophotonics, high-vacuum and atomic physics might be able to bring.

## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+MN+NS-TuA

## 2D Device Physics and Applications

Moderator: Roland Kawakami, The Ohio State University

2:20pm **2D+EM+MI+MN+NS-TuA1 Spin Relaxation and Proximity Effect in WS<sub>2</sub>/Graphene/Fluorographene Non-local Spin Valves**, Adam Friedman, Laboratory for Physical Sciences; K.M. McCreary, J.T. Robinson, O.M.J. van 't Erve, B.T. Jonker, US Naval Research Laboratory

The mechanisms leading to spin relaxation in graphene and its heterostructures continue to be debated. Control of the spin relaxation in graphene-based structures is necessary to achieve the envisioned utility of graphene in future spintronic devices beyond Moore's law. Proximity induced spin relaxation caused by contact to a high spin-orbit material, such as WS<sub>2</sub>, offers a promising avenue to manipulate the spin lifetime [1]. We demonstrate the operation of WS<sub>2</sub>/graphene/fluorographene non-local spin valves and extract the spin lifetimes for a range of carrier concentrations by Hanle effect measurements. Four-terminal charge transport measurements allow us to calculate the momentum relaxation time as a function of carrier concentration and compare it to the spin lifetime. These data show that the D'yakonov-Perel' mechanism is the dominant spin relaxation mechanism for WS<sub>2</sub>/graphene/fluorographene devices, while, for reference graphene/fluorographene devices, linear scaling between the spin and momentum lifetimes points to spin-flip scattering during strong elastic scattering events where the scattering event is strongly coupled to the electron spin. We attribute the change in spin relaxation type in part with the inclusion of WS<sub>2</sub> as a substrate to proximity induced spin-orbit coupling due to the adjacent WS<sub>2</sub> layer, and we compare our data to the literature.

[1] A.L. Friedman, et al. Carbon 131, 18-25 (2018).

2:40pm **2D+EM+MI+MN+NS-TuA2 Two-dimensional Field-effect Light Emitting Transistors**, Junyoung Kwon, H. Ryu, Yonsei University, Republic of Korea; J.Y. Lee, C.H. Lee, Korea University, Republic of Korea; G.H. Lee, Yonsei University, Republic of Korea

Two dimensional (2D) materials and their heterostructures hold great promises in various applications due to their unique properties and newly discovered physics. Especially, high exciton binding energy and emergence of charged excitons, *i.e.* trions, have shown that 2D semiconductors, such as transition metal dichalcogenides (TMDs), are promising candidates for new concept optoelectronics. Although lots of optoelectronic devices based on the van der Waals heterostructures of 2D materials, such as photodetectors, solar cells, and light emitting devices, have been demonstrated, development of novel optoelectronic devices is still required to fully utilize unique properties of 2D materials and enable multi-functions and versatile applications. Here we demonstrate 2D field-effect light emitting transistors (2D-FELET) consisting of monolayer WSe<sub>2</sub> (light-emitting channel layer) and graphene contacts (tunable carrier injection electrodes). We encapsulated monolayer WSe<sub>2</sub> with two pieces of hexagonal boron nitride and fabricated graphene contacts to two ends of WSe<sub>2</sub>. To selectively inject different types of charge (electrons and holes) at two graphene contacts, two separate top gates on top of WSe<sub>2</sub>-graphene overlap regions were fabricated. By independent modulation of two top gates, Schottky barrier heights for electrons and holes can be tuned, which enables the selective charge injections. When two top gates are oppositely biased, electrons can be injected from one end of WSe<sub>2</sub> channel and holes can be injected from the other end. These opposite charges are recombined at the middle of WSe<sub>2</sub> channel, leading to strong light emission. The performance of the 2D-FELETs is tunable by additional electrical field from back gate. Furthermore, the devices produced in this work can be used as polarity-tunable FETs and photodetectors, simultaneously, which are beneficial for further CMOS integration. Our study shows great potential of 2D-FELETs toward future optoelectronic applications, which request ultra-thinness, transparency, flexibility, high efficiency, multi-functions, and high integration.

3:00pm **2D+EM+MI+MN+NS-TuA3 Quantum Devices with 2D Materials**, H. Overweg, M. Eich, R. Pisoni, T. Ihn, P. Rickhaus, ETH Zurich, Switzerland; Klaus Ensslin, ETH Zürich, Switzerland

INVITED

Quantum dots in graphene have been mostly realized by etching. This leads to localized states at the uncontrolled edges dominating the transport properties of these quantum devices. [1] It is well known that in bilayer graphene gaps can be opened by vertical electrical fields. [2] This approach has been used with limited success to define quantum devices [3]. The

pinch-off characteristics are typically limited by leakage currents often thought to occur at the physical sample edges [4].

Here we demonstrate that electrostatically tunable barriers can be fabricated on bilayer graphene devices with graphite as a back gate. We measure pinch-off resistances exceeding GΩms and observe quantized conduction plateaus for one-dimensional constrictions. [5] With suitable gate arrangements few carrier hole and electron quantum dots can be electrostatically defined. We measure the controlled occupation of quantum dots with single holes and electrons. Four-fold level bunching is observed in Coulomb blockade spectroscopy which is understood in terms of valley and spin states. Magnetic field dependence allows to investigate orbital and spin/valley degrees of freedom.

We further demonstrate quantum devices build on MoS<sub>2</sub>.

1. For a review see Bischoff et al., Applied Physics Reviews 2, 031301 (2015)
2. Oostinga et al., Nat. Materials 7, 151 (2007)
3. Allen et al., Nat. Comm. 3, 934 (2012)
4. [<https://www.nature.com/articles/ncomms14552#auth-1>] et al., Nat. Comm. 8, 14552 (2017)
5. Overweg et al., [<https://arxiv.org/abs/1707.09282>], [<https://arxiv.org/abs/1709.00870>]

4:20pm **2D+EM+MI+MN+NS-TuA7 GaN Microdisk Light-emitting Diode Display Fabricated on Graphene**, Youngbin Choe, K. Chung, K. Lee, M.S. Song, J.B. Park, H. Kim, J.Y. Park, G.-C. Yi, Seoul National University, Republic of Korea

Microdisplay with high resolution, brightness, and efficiency with long-term stability and reliability are highly required for advanced display technologies. Inorganic semiconductor LEDs best suits this purpose because they can emit very high density of light from a small area and they have very high efficiency and long-term stability. To use inorganic LEDs for display applications, various lift-off and transfer techniques of inorganic thin films grown on single crystal substrates, such as sapphire or Si, were developed. However, achieving display devices using inorganic semiconductor thin films is still very challenging because of the limited size and high manufacturing cost of the single crystal substrates, as well as the complicated processes required for lift-off and assembly. To resolve this problem, growths of inorganic semiconductor nanostructures and thin films on graphene substrates have recently been proposed, since graphene has great scalability and extremely thin layered hexagonal lattice structure as an excellent substrate for GaN growth. Moreover, the inorganic semiconductors prepared on large-area graphene can be transferred easily to or grown on elastic substrates to meet the flexibility demand. Here, we suggest a method of fabricating ultrathin, high-resolution inorganic microdisplay based on individually addressable GaN microdisk LED arrays grown on graphene dots.

Here, we report on the fabrication and EL characteristics of ultrathin and individually addressable GaN microdisk LED arrays grown on graphene dots for microdisplay applications. GaN microdisks were prepared by epitaxial lateral overgrowth on patterned graphene microdots on SiO<sub>2</sub>/Si substrates using MOVPE. After preparing the GaN microdisk arrays, *p*-GaN and InGaN/GaN multiple quantum well, and *n*-GaN layers were heteroepitaxially grown on the surface of the GaN microdisks. Ultrathin layers composed of GaN microdisk LED arrays on graphene dot were prepared by coating a polyimide layer and lifting-off the entire layers from the substrate. Then, single-walled carbon nanotubes (SWCNTs)/Ni/Au and SWCNTs/Ti/Au multiple electrode lines were formed on the top and bottom surface of GaN microdisk arrays in an aligned manner and crossing each other. The electrical and optical characteristics of the individually addressable GaN microdisk array on graphene dots were investigated by measuring their *I*-*V* curves and EL characteristics at various bending conditions. We also confirmed that the ultrathin micro-LED display worked reliably under flexible conditions and continuous operation mode.

4:40pm **2D+EM+MI+MN+NS-TuA8 Room Temperature Magnetron Sputtering and Laser Annealing of Ultrathin MoS<sub>2</sub> for Transistor Device Fabrication on Flexible Polymer Substrates**, Benjamin Sirota, University of North Texas; N.R. Glavin, Air Force Research Laboratory; C. Arnold, A.A. Voevodin, University of North Texas

Pulsed magnetron sputtering and subsequent laser annealing provide technologically attractive scalable route for producing two-dimensional (2D) semiconducting grade MoS<sub>2</sub> materials directly on the surface of flexible polymer substrates. In this study the room temperature magnetron sputtering was used to deposit 10 nm thick, amorphous MoS<sub>2</sub> films on

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flexible PDMS as well as rigid SiO<sub>2</sub>/Si substrates. This was followed by 248 nm pulsed laser annealing to produce polycrystalline 2H-MoS<sub>2</sub> over large areas. Raman and XPS analysis confirmed that pulsed laser annealing with about 1 mJ/cm<sup>2</sup> energy density had induced film crystallization from amorphous to hexagonal, while preserving MoS<sub>2</sub> chemical composition, and avoiding formation of oxide phases or damage to the temperature-sensitive polymer surface. Electrical measurements confirmed an order of magnitude improvement in electrical conductivity of the laser annealed films as compared to amorphous MoS<sub>2</sub>. Top-gated field effect transistor (FET) devices with laser annealed sputter grown MoS<sub>2</sub> were directly fabricated on PDMS surfaces. Oxygen substitution of sulfur in sputter deposited MoS<sub>2</sub> and polycrystallinity of the laser annealed 2H-MoS<sub>2</sub> films resulted in low mobility values when compared to mechanically exfoliated and chemical vapor deposition grown single-crystal 2D MoS<sub>2</sub>. However, the described approach is intrinsically scalable and provides a direct growth route for the fabrication of 2D transition metal dichalcogenide semiconducting devices on the surface of flexible and stretchable polymers.

5:00pm **2D+EM+MI+MN+NS-TuA9 Black Phosphorus: Fundamental Properties and Emerging Applications**, *Han Wang*, University of Southern California **INVITED**

In this talk, I will discuss our recent work in developing novel electronic and photonic devices based on the anisotropic properties of black phosphorus (BP) and its isoelectronic materials such as the monochalcogenides of Group IV elements. High mobility, narrow gap BP thin film (0.3 eV in bulk) fill the energy space between zero-gap graphene and large-gap TMDCs, making it a promising material for mid-infrared and long wavelength infrared optoelectronics. Most importantly, its anisotropic nature within the plane of the layers allow for the realization of conceptually new electronic and photonic devices. Here, I will first present our work in understanding the fundamental electronic and optical properties of black phosphorus using a newly developed scanning ultrafast electron microscopy (SUEM) technique and photoluminescence spectroscopy. Our recent study of bandgap tuning in BP and the demonstration of a polarization sensitive BP mid-IR detector will then be presented. In the second half of my talk, I will discuss our work on developing two dimensional materials based artificial synaptic devices for neuromorphic electronics, including emulating the heterogeneity in synaptic connections using the anisotropic properties of BP and a tunable memristive device as a reconfigurable synapse. I will conclude with remarks on promising future research directions of low-symmetry electronics based on anisotropic 2D materials and how their novel properties is expected to benefit the next-generation electronics and photonics technologies.

5:40pm **2D+EM+MI+MN+NS-TuA11 Patterned Growth of Hybrid Bulk-2D Tungsten Diselenide for Transistor Applications**, *Quinten Yurek, I. Liao, D. Barroso, A.E. Nguyen, N. Duong, G. Stecklein, L. Bartels*, University of California, Riverside

As device dimensions shrink, surfaces and interfaces between materials make up a larger volume fraction of a device leading to degrading device properties in 3D materials. One solution is to use 2D materials, however these materials introduce additional challenges. For instance, high resistance Schottky barriers and a small number of free charge carriers in comparison to bulk materials. The effective mobility of field effect transistors (FETs) based on two-dimensional (2D) single-layer transition metal dichalcogenide (TMD) films is frequently limited by barriers at the contacts, as opposed to the native properties of the TMD material. Specifically, high resistance Schottky barriers form at the TMD/metal interface because of the film's thinness and resulting small number of carriers. Here we demonstrate a scalable single-step deposition method for nanoscale hybrid 2D/3D TMD structures encoded by lithographic patterning prior to deposition. By confining the metal contact to the bulk regions of WSe<sub>2</sub>, the effective mobility is increased to nearly 100 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup> with an on/off ratio >10<sup>5</sup> for bottom-gated devices (through 300nm of oxide), even for comparatively long channels (>5 microns) and absent other contact optimization. Our process involves lithographic patterning of a hafnium (IV) dioxide film onto the SiO<sub>2</sub>/Si substrate prior to TMD growth. Bulk-like 3D WSe<sub>2</sub> is observed to grow at the location of the hafnia, while 2D single-layer material is grown in regions of bare SiO<sub>2</sub>. Systematic evaluation of transport data allows us to extract Schottky barrier heights and other fundamental properties of our hybrid devices. We demonstrate that this process can be used to create devices with metal/3D TMD contacts, which exhibit a reduced Schottky barrier height, while continuing to use 2D TMD channels, which result in an excellent on-off ratio.

6:00pm **2D+EM+MI+MN+NS-TuA12 Enhanced Ionic Sensitivity in Solution-Gated Graphene-Hexagonal Boron Nitride Heterostructure Field-Effect Transistors**, *A.D. Radadia, Nowzesh Hasan, B. Hou, A.L. Moore*, Louisiana Tech University

The charge transport in solution-gated graphene devices is affected by the impurities and disorder of the underlying dielectric interface and its interaction with the solution. This paper reports advancement in field-effect ion sensing by fabricating a dielectric isomorph, hexagonal boron nitride between graphene and silicon dioxide of a solution-gated graphene field effect transistor. Ionic sensitivity of Dirac voltage as high as -198 mV/decade for K<sup>+</sup> and -110 mV/decade for Ca<sup>2+</sup> were recorded. Increased transconductance due to increased charge carrier mobility was accompanied with larger ionic sensitivity of the transconductance due to larger ionic sensitivity of the charge carrier mobility. These findings define a standard to construct future graphene devices for biosensing and bioelectronics applications.

**Manufacturing Science and Technology Group  
Room 202B - Session MS+MN-TuA**

**IoT Session: Challenges of Sensor Manufacturing for the IoT**

**Moderator:** Robert Lad, University of Maine

2:20pm **MS+MN-TuA1 Manufacturing Strategies for Flexible Hybrid Electronics**, *Scott Miller*, NextFlex **INVITED**

Flexible Hybrid Electronics (FHE) combines technologies and manufacturing capabilities from the worlds of printing and additive manufacturing; flexible, bendable, stretchable, and 3D substrates; and conventional silicon integrated circuits to bring novel form and function to high-performing electronic devices. The US manufacturing ecosystem for FHE is rapidly growing and applications of FHE devices are being advanced in areas as diverse, and yet overlapping, as human health and performance monitoring, antennas and wireless communications, soft robotics, structural health management, and IoT. A single device build can require solving substrate challenges, printing functional conductors, resistors, and dielectrics, placing discrete passives, attaching bare-die integrated circuits using conductive adhesives, integrating a power supply, and encapsulating the entire device. As a Manufacturing Institute, NextFlex works with its members on technologies that have passed the applied research stage to advance their readiness for manufacturing and position them for product development. This talk will explore challenges and opportunities in FHE, including translating designs to manufacturing, material and device characterization, availability of material and process data, and scaling processes to high-rate manufacturing. Approaches to address these challenges will be discussed and example projects related to IoT will be presented.

3:00pm **MS+MN-TuA3 Enabling Smart and Connected Living through High Volume Roll to Roll Manufacturing**, *Enid Kivuti*, Sheldahl Flexible Technologies **INVITED**

Enabling Smart and Connected Living through High Volume Roll to Roll Manufacturing

The presentation will provide an overview of automated, continuous processing technologies available in the manufacture of Flexible Printed Electronics for the Internet of Things applications. Beginning with material choice, and concluding with proposed useable devices, we will explore Additive, Subtractive and Hybrid technologies and the governing design rules. We will review recent industry developments that enable finished products to improve user experience. Finally, we will provide examples of scalable IOT applications that meld the use of existing capital assets with the rapidly evolving industry options to deliver improved performance at a lower total cost of ownership.

Key Words:

Thin Film Vacuum Deposition

Printed Electronics

Hybrid Technology

Sensors

Medical

Automotive

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4:20pm **MS+MN-TuA7 New Generation Chemical and Biological Sensors: From New Ideas to Manufacturable Products in the era of Internet of Things and Industrial Internet**, *Radislav Potyrailo*, General Electric Global Research Center

INVITED

Modern monitoring requirements of gases and liquids for demanding applications such as medical diagnostics, environmental surveillance, biopharmaceutical process control, industrial safety, and homeland security push the limits of existing detection concepts where we may reach their fundamental performance limits. Thus, without violating the laws of physics, chemistry, and electronics, we need to develop new practical detection concepts and instruments. We are developing new generation of handheld, wireless, and wearable sensors that bridge the gap between the existing and required sensing capabilities. This talk will stimulate your scientific and engineering senses by posing several fundamental and practical questions on principles of chem/bio sensing and by demonstrating on how we address these questions in the developments of sensors with previously unavailable capabilities with examples of strategies of bringing new ideas from their initial lab tests, to field validation, and to final products.

5:00pm **MS+MN-TuA9 The Unique Challenges Implantable Sensor Manufacture**, *Kimberly Chaffin, S. Terry*, Medtronic plc

INVITED

Sensors onboard today's implantable medical devices monitor the critically ill and trigger the delivery of life sustaining and saving therapies. As medicine moves from retrospective treatment to predict and prevent, a transition enabled, in part, by the Internet of Things (IoT), sensors will no longer only be operational in the critically ill, but in all of us. In the future, sensors will have the sole purpose of measuring physiological signs and providing patient centric feedback to prevent future events. Setting aside the psychological challenges of receiving a long-term implant for prevention, this transition to prevent and predict is making the medical device industry rethink sensor manufacture, where the device-biological interface is one of several critical factors. The current design paradigm of isolating implantable device circuitry from the biological environment in hermetic titanium cans, largely limiting the signal to electrical feedthroughs, must shift to allow for new sensor modalities. Chemical sensors must detect biomarkers unhindered by the immune response that accompanies every implant. Optical sensors must 'see' into the body. Pressure sensors must employ sensitive diaphragms where the internal device pressure must remain constant and the fibrotic capsule formation associated with the immune response must not dampen sensitivity. In this talk, we will review the critical manufacturing technologies being developed for implantable sensors that predict and prevent.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+AM+MI+MN+SS+TR-TuA

### SPM – Probing and Manipulating Nanoscale Structures

**Moderators:** Renu Sharma, NIST Center for Nanoscale Science and Technology, Carl Ventrice, Jr., SUNY Polytechnic Institute

2:20pm **NS+AM+MI+MN+SS+TR-TuA1 Building Artificial Quantum Matter with Dopant Atoms**, *Sven Rogge*, University of New South Wales, Australia

INVITED

Atomic-scale engineering reached the level of control where single-atom devices can be reproducibly fabricated with high yield. This talk focuses on the progress of single dopant atom placement in the context of engineered quantum matter. Silicon offers a particularly interesting platform for single dopants because when isotopically purified it acts as a "semiconductor vacuum" for spins. This leads to extraordinary coherence that is used to realise donor atom based qubits. Spatially resolved tunnelling experiments reveal the spectrum and quantum state image of single atoms and tunnel coupled arrangements of atoms. These measurements grant access to the wavefunction of donors in the silicon lattice that makes it possible to pinpoint the dopants to their exact position in the lattice that is essential in the evaluation of engineered quantum matter. A first step towards engineered Hamiltonians for Fermionic systems in the form of atomic chains was taken where interacting dopants were employed to simulate a two-site Hubbard Hamiltonian at low effective temperatures with single-site resolution. Quasi-particle tunnelling maps of spin-resolved states with atomic resolution reveal interference processes from which the entanglement entropy and Hubbard interactions are quantified. We will present dopant based multi-electrode devices fabricated by the scanning probe hydrogen depassivation and decoration technique where the quantum state of the device can be manipulated and imaged in situ. The

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aim of this work is to build a two dimensional array of up to 30 spins in the solid state to implement complex highly correlated systems.

3:00pm **NS+AM+MI+MN+SS+TR-TuA3 Scanning Tunneling Microscopy Study of Structure Control of a Nanocarbon Catalyst through a Surface-Activated coupling Reaction**, *Jeremy Schultz, P. Whiteman, N. Jiang*, University of Illinois at Chicago

In order to optimize nanocarbon materials for metal-free catalysis, the structure must be controlled and characterized at the nanoscale. One method for the bottom-up assembly of nanocarbon catalysts is through an Ullmann-type coupling reaction induced by a metal substrate, where a halide leaving group allows covalent intermolecular coupling. Scanning tunneling microscopy has been applied to a fundamental study of 3,6-dibromo-phenanthroquinone (DBPQ), a molecule selected for its catalytically active diketonic groups. Conjugated polymers formed from DBPQ have been found to be capable of catalyzing alkane oxidative dehydrogenation (ODH) reactions as well as nitrobenzene (NB) reduction reactions.

Different surfaces were investigated for their role in the surface-activated coupling reaction. Intact monomer molecules were found to self-assemble through hydrogen and halide interactions on Ag(100), resulting in well-packed molecular islands which impacted the organometallic structure ultimately formed after reaction. On Au(100), two competing intermediate dimers were observed resulting from a chiral covalent bond between base DBPQ molecules. Cis dimers were found to result in reaction products that became stuck as tetramers without the potential for further polymerization. Utilization of increasing coverage and a new surface identity that arose from the leaving Bromide resulted in selective formation of longer conjugated polymer chains composed of trans dimers. This study characterizes the ability of initial self-assembly and leaving groups to steer reaction dynamics and control the structure of a nanocarbon catalyst.

3:20pm **NS+AM+MI+MN+SS+TR-TuA4 Detecting the Tip Shape Dependence of the Plasmonic Photon Emission under STM**, *Songbin Cui*, Pohang University of Science and Technology, Republic of Korea; *U. Ham*, Institute for Basic Science (IBS), Republic of Korea; *T.-H. Kim*, Pohang University of Science and Technology, Republic of Korea

Photon signal can be enhanced significantly by modifying the plasmonic nanocavity. This enhancement becomes an important issue in super-resolution microscopy and high resolution spectroscopy, such as scanning tunneling microscopy (STM) electroluminescence [1], surface enhanced Raman spectroscopy, tip enhanced Raman spectroscopy [2], and so on. Low temperature STMs can allow us to achieve less than 1nm tip-sample gap stably. This gap-mode plasmonic nanocavity between an STM tip and surface realizes sub-molecular photon spectroscopy [1]. A few works demonstrated that light emission signal can be effectively enhanced by certain resonant plasmonic spectral peaks, which can be modified by tip indentation [2] and showed theoretically that the larger tip aperture causes a blue shift and the sharper apex curvature results in higher intensity in a photon spectrum [3]. However, the tip shape dependence of the plasmonic nanocavity remains unclear. In this work, we experimentally present the role of tip shape in surface plasmonic light emission. We have used Ag tips and a Ag(100) substrate, and photon signals have been measured from both side of the STM tip simultaneously. We dipped STM tips into the substrate with controlling the dipping depth and the lifting speed in order to change the tip shape, and then, the tip shape subsequently was checked through STM profiles. We found that changing small parts of tip apex (<3nm tip direction) can differ the photon spectrum significantly. Furthermore, the plasmonic photon emission from different direction from a STM tip could be quite different due to tip shape asymmetry. This finding can help us to tune the plasmonic photon emission spectra more efficiently.

[1] R. Zhang et al., Nature 498, 82–86 (2013).

[2] Z. C. Dong et al., Nature Photonics 4, 50–54 (2010).

[3] J. Aizpurua et al., Physical Review B 62, 2065-2073 (2000).

4:20pm **NS+AM+MI+MN+SS+TR-TuA7 Advances in SPM Methods for Energy-relevant Materials**, *Marina Leite*, University of Maryland College Park

INVITED

The scientific understanding of nanoscale materials and devices is continuously growing ever since atomic force microscopy (AFM) has enabled us to image these systems at similar length scale. Specifically, there is a pressing need for functional imaging as energy-relevant technologies are becoming dominated by nano- and mesoscale constructs. In this presentation I will review my group's recent research discoveries

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based on new AFM methods to measure and determine how the electrical, chemical, and/or optical properties influence overall photovoltaic device behavior [1,2]. We realize novel functional imaging AFM-based methods to elucidate the driving forces for the dynamic response of the perovskites upon and post-illumination [3], and polycrystalline materials for solar cells [4,5]. We map nanoscale variations in open-circuit voltage  $V_{oc} > 300$  mV under 1-sun illumination, not revealed by conventional AFM tools. Using fast-KPFM (16 seconds/scan) while maintaining high spatial sensitivity, we map, in real-time, the dynamics of the  $V_{oc}$  in perovskite solar cells with spatial resolution  $< 100$  nm. Unexpectedly, we identify a 'residual  $V_{oc}$ ' post-illumination, attributed here to iodine ion migration, a process that takes place in a time scale of several minutes. We foresee our functional imaging tool to be implemented in the identification of stable perovskite compounds, ranging from lead-free and non-toxic alternatives to new options for tandem designs.

[1] *ACS Energy Letters* **2**, 2761 (2017). [Invited Review](#).

[2] *ACS Energy Letters* **2**, 1825 (2017). [Invited Perspective](#)

[3] *Nano Letters* **17**, 2554 (2017).

[4] *ACS Energy Letters* **1**, 899 (2016).

[5] *Advanced Energy Materials* **5**, 1501142 (2015).

5:00pm **NS+AM+MI+MN+SS+TR-TuA9 Coherent Electrical Contact to Semiconducting Graphene Nanoribbon**, *Chuanxu Ma, L. Liang*, Oak Ridge National Laboratory; *Z. Xiao*, North Carolina State University; *A.A. Puzetzyk, K. Hong*, Oak Ridge National Laboratory; *W. Lu, J. Bernholc*, North Carolina State University; *A.-P. Li*, Oak Ridge National Laboratory

High quality electrical contact to low-dimensional semiconductor channel materials is the key to unlocking their unique electronic and optoelectronic properties for fundamental research and device applications. Inappropriate contacts create interfacial states that can pin the Fermi level and form a large Schottky barrier. For 2D transition metal dichalcogenides (TMDs), a route to a high-performance contact has recently been proposed by using a phase transition that converts a hexagonally packed semiconductor (2H) phase into a distorted octahedrally packed metallic (1T') phase. However, a similar approach is not available for 1D materials. Conceptually, an ideal contact would be a metal-semiconductor interface formed with native covalent bonds without introduction of any structural or electronic boundaries. Realization of such a seamless contact in 1D materials such as graphene nanoribbons (GNRs) requires atomically precise development of a heterostructure from well-defined atomic or molecular precursors.

Here we report on a successful approach for making seamless contacts in 1D materials through the formation of GNR staircase heterostructure. The coherent staircase is made of GNRs with widths varying from 7, 14, 21 and up to 56 carbon atoms. The graphitic heterostructures are synthesized by a surface-assisted self-assembly process with a single molecular precursor. While the 7-atom-wide GNR is a large-gap semiconductor, the conjugated wide GNRs are either quasi-metallic or small-gap semiconductors, similarly to the 2D metals. Our study, which combines STM and Raman measurements with DFT calculations, reveals that the heterointerface consists of native  $sp^2$  carbon bonds without localized interfacial states. Such a seamless heterostructure offers an optimal electrical contact to the wide-gap 1D semiconductor.

5:20pm **NS+AM+MI+MN+SS+TR-TuA10 Visualizing Coordination Structures of Small Gas Molecules to Metallo-porphyrin on Au(111) Using Scanning Tunneling Microscopy**, *MinHui Chang*, Korea University, Republic of Korea; *Y.H. Chang, N.Y. Kim*, Korea Advanced Institute of Science and Technology (KAIST); *U.S. Jeon, H. Kim*, Korea University, Republic of Korea; *Y.-H. Kim*, Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea; *S.-J. Kahng*, Korea University, Republic of Korea

Binding reaction between small molecules and metallo-porphyrins play crucial roles in functional processes of biological systems such as oxygen delivery, muscle contraction, and synaptic transmission. Their geometrical structures such as tilted binding of NO to metallo-porphyrin have been recently confirmed by high-resolution scanning tunneling microscopy (STM) images at the single molecule level. Here, we present STM images of further systems, di, tri, and quadra-atomic small molecules, coordinated to metallo-porphyrin on Au(111). We observed square ring, rectangular ring, and center-bright structures for three different small molecules. With the help of density functional theory (DFT) calculations, we reproduce the experimental STM images in the simulated images. Thus, our study shows that geometric structures of small molecules coordinated to metallo-porphyrins can be probed with STM combined with DFT methods.

5:40pm **NS+AM+MI+MN+SS+TR-TuA11 Effects of Dimensionality on the Reactivity of Carboxylic-Acid-Terminated Monolayers**, *Dominic Goronzy<sup>1</sup>, E. Avery, N.M. Gallup*, University of California, Los Angeles; *J. Staněk, J. Macháček, T. Baše*, Institute of Inorganic Chemistry, Academy of Sciences of the Czech Republic; *K.N. Houk*, Chemistry and Biochemistry, University of California, Los Angeles; *P.S. Weiss*, University of California at Los Angeles

Self-assembled monolayers (SAMs) are an advantageous construct to modify surfaces and thereby to tune material properties. Three major determinants affect the spontaneous assembly of monolayers: the substrate-monolayer interface, the interactions between the adsorbate molecules, and the monolayer-environment interface. By controlling the exposed functional groups in the SAM, this interface between the surface and the environment can be probed and manipulated. To examine how exposed carboxyl functional groups modulate the properties of SAMs, we have tethered thiol-functionalized carborane cage molecules with and without a carboxyl group to Au{111} surfaces. Using scanning tunneling microscopy (STM), visualization of the *para*-functionalized carboxylic acid carboranethiol was only possible in the form of a mixed monolayer of functionalized and unfunctionalized molecules. These experiments demonstrated that the functionalized molecule adopted the same nearest-neighbor spacings on the surface as the unfunctionalized *para*-carboranethiol, approximately 7.2 Å. By comparison, in our study of carboranethiols with a carboxylic acid functional group attached in the *meta* position, we have been able to image pure functionalized monolayers via STM with these molecules showing nearest-neighbor spacings of 8.4 Å, approximately 1 Å larger than the unfunctionalized carboranethiols. Studies of two different isomers of *meta*-carboranethiolate carboxylic acids yielded similar results. In order to examine the effects of changing dimensionality from a 3D solvent system to a 2D thin film, we applied contact angle titration to probe the reactivity of the carboxylic acid head group. These experiments demonstrated a substantial shift from a  $pK_a$  of 3-3.2 in solution (3D) to an apparent surface  $pK_a$  of approximately 6.5-7.5. Density functional theory calculations were performed to test the effects of desolvation by 2D confinement and showed shifts in  $pK_a$  consistent with the experimental data. Together, these results support the concept that the confinement in a 2D environment induces significant changes in reactivity in the molecules, as evidenced by the  $pK_a$  shift. Thus, precise positioning of functional groups in SAMs is an important tool to investigate the behavior of surface-confined molecules. This system may also serve as a model to explore dimensionality effects in biological systems, including proteins confined within membranes.

<sup>1</sup> NSTD Student Award Finalist

## MEMS and NEMS Group

### Room 202B - Session MN+NS+PS-WeM

#### IoT Session: Multiscale Manufacturing: Enabling Materials and Processes

**Moderators:** Susan Burkett, The University of Alabama, Sébastien Hentz, CEA/LETI-University Grenoble Alpes, France

8:00am **MN+NS+PS-WeM1 Miniaturizing 3D Printed Microfluidics: State-of-the-Art and Outlook**, *Greg Nordin*, Brigham Young University **INVITED**  
While there is great interest in 3D printing for microfluidic device fabrication, the challenge has been to achieve feature sizes that are in the truly microfluidic regime ( $<100\ \mu\text{m}$ ). The fundamental problem is that commercial tools and materials, which excel in many other application areas, have not been developed to address the unique needs of microfluidic device fabrication. Consequently, we have created our own stereolithographic 3D printer and materials that are specifically tailored to meet these needs. We show that flow channels as small as  $18\ \mu\text{m} \times 20\ \mu\text{m}$  can be reliably fabricated, as well as compact active elements such as valves and pumps. With these capabilities, we demonstrate highly integrated 3D printed microfluidic devices that measure only a few millimeters on a side, and that integrate separate chip-to-world interfaces through high density interconnects (up to 88 interconnects per square mm) that are directly 3D printed as part of a device chip. These advances open the door to 3D printing as a replacement for expensive cleanroom fabrication processes, with the additional advantage of fast (30 minute), parallel fabrication of many devices in a single print run due to their small size.

8:40am **MN+NS+PS-WeM3 A Novel Inkjet Printing Technology Based on Plasma Conversion of Metal-Salt Based Inks for the Fabrication of Microfabricated Sensors**, *Y. Sui, R.M. Sankaran, Christian Zorman*, Case Western Reserve University

Inkjet printing is a leading additive manufacturing method to produce patterned metal thin films on flexible substrates. The most commonly-used inks consist of colloidal nanoparticle suspensions that employ organic molecules to stabilize the nanoparticles from agglomeration and precipitation. High temperature ( $>200^\circ\text{C}$ ) treatment is used after printing to remove the insulating organics and sinter the nanoparticles. The thermal step can limit printing on polymers such as PDMS, paper, and other temperature-sensitive substrates. Moreover the selection of metals is limited by those available in nanoparticle suspensions, with the most popular being Ag.

In this paper, we present the development of an ink-jet printing process that uses a particle-free, stabilizer-free ink and low-temperature plasma to produce electrically conductive metallic patterns on temperature-sensitive substrates. The inks are comprised of a metal salt, a solvent, and a viscosity modifier tailored to enable printing using a Dimatix DMP3000 series printer. The as-printed structures are treated with a low-pressure argon plasma which serves to convert the metal salt-based structures to metal structures with conductivities that approach bulk values. To date, we have demonstrated the process for Sn, Pb, Bi, Cu, Pt, Ag, Pd, and Au-based inks. The plasma-treated structures exhibit a high degree of porosity that can be as high as 70%, making them particularly well suited for use as active elements in microfabricated sensors. The extended paper will present details pertaining to the printing process, material characterization and testing of mechanical, chemical and biological sensors fabricated by this printing process.

9:00am **MN+NS+PS-WeM4 Full Wafer Thickness Through Silicon Vias for MEMS Devices**, *Andrew Hollowell, E. Baca, D. Dagel, M.B. Jordan, L. Menk, K. Musick, T. Pluym, J. McClain*, Sandia National Laboratories

A significant amount of development has been achieved integrating TSVs with standard silicon (Si) substrates; however, there are unique challenges associated with integrating TSVs with MEMS substrates. Industry has achieved TSV integration through a dependence on substrate thinning, a TSV reveal approach. However, often these MEMS devices depend on the thickness of the substrate for controlling the radius of curvature of the substrate, such as throughout Sandia's ultra-planar multilevel MEMS technology (SUMMIT™). TSV filling relies on tight control of the fluid kinetics during the electroplating process and the ability to balance the diffusion of  $\text{Cu}^{2+}$  and organic suppressor molecules throughout the depth of the via in order to realize a void-free fill of the TSV. In this work we have

extended the filling model for  $60\ \mu\text{m}$  deep TSVs, developed by Tom Moffat and Dan Josell, up to  $675\ \mu\text{m}$  deep TSVs.

In addition to the thickness constraints for MEMS integration, often MEMS devices are realized through unique release processes and are dependent on high temperature anneals. The most common release process is a hydrofluoric acid (HF) based release to selectively remove supporting oxide films and preserve the Si features that make up the MEMS components. The necessity to release structure in selective etchants presents additional challenges for integrating TSVs with MEMS components. We have overcome this challenge through the integration of additional capping layers which are selectively removed after the MEMS release. In order to accommodate the need for high temperature anneals we have removed the use of metal in the MEMS device and instead used doped silicon. The Cu TSVs are then integrated with the device after all the high temperature anneals are complete, making direct electrical contact to the doped Si. In this work, we present our integration approach for mating Cu TSVs with doped Si MEMS contacts and our plating approach for superfilling  $675\ \mu\text{m}$  deep,  $100\ \mu\text{m}$  wide TSVs.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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9:20am **MN+NS+PS-WeM5 Scaling from Die Level to Full 150 mm Wafer TSV Filling through Fluid Dynamics Modeling and Current Controlled Deposition**, *Ehren Baca, M.B. Jordan, L. Menk, K. Musick, P. Yeh, A.E. Hollowell*, Sandia National Laboratories

In this work we have developed a novel methanesulfonic acid (MSA) based electrolyte with a single suppressor additive for filling  $100\ \mu\text{m}$  diameter  $675\ \mu\text{m}$  deep through silicon vias (TSVs). Contrary to conventional three-additive systems we have achieved bottom up super filling of these large TSVs with a single suppressor additive. This bottom up super filling mechanism is dependent on a strict balance between applied potential and diffusion of both suppressor molecules and  $\text{Cu}^{2+}$  ions. The bottom up deposition was developed through die level plating experiments on sample sizes approximately  $1\ \text{in}^2$ . We control the solution replenishment by connecting the sample, both electrically and mechanically, to an aluminum rod and rotating the sample in solution. The rotation rate is directly correlated to the velocity of solution moving across the opening of the vias and therefore related to the solution replenishment inside the TSVs. At first a potentiostatic approach was used to supply a sufficient potential to break down the suppressor with a reference electrode in our plating cell.

Mapping the current, during deposition allowed us to develop a galvanostatic plating process.

Experiments were performed to scale this plating process to be compatible with production level electroplating tools. The fluid dynamics and applied current are significantly different on production plating tools. The tools do not come equipped with reference electrodes and in some cases, they have multiple anodes for current partitioning to control the uniformity of the electric field. Further, the wafer rotates about the center of the wafer and baffles are integrated into the tool to control the uniformity of a fountain type fluid replenishment system. With the wafer rotated about its center, there is a large variance in the velocity of fluid at different radii along the wafer. In this work, we present a set of scaling experiments performed on die with incremental increases in sample size to clearly map the die level plating parameters to a full wafer plating tool and achieve uniform TSV filling across a  $150\ \text{mm}$  wafer.

This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

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9:40am **MN+NS+PS-WeM6 Batch Level Electroless Under Bump Metallization for Singulated Semiconductor Die**, *Matthew Jordan, E. Baca, J. Pillars, C. Michael, A.E. Hollowell*, Sandia National Laboratories

Multi project-wafers (MPWs) allow multiple customers to share the cost of a manufacturing run from an advanced semiconductor foundry. This offers a cost-effective solution for low volume the fabrication or prototyping of application specific integrated circuits (ASICs). This practice is especially appealing for those in academia or government that often only require small quantities of devices for research or niche applications. With many products on a wafer, all the products must adhere to the same strict design rules. In practice this means that the final metallization is made using AlCu. This presents challenges for advanced packaging of MPW die as AlCu is not compatible with conventional flip chip solder because of oxidation of the AlCu metal. Further complicating the integration of MPW die is the fact that they are singulated prior to delivery, preventing the use of lithography, and thus ruling out the deposition and patterning of solder-compatible metals over the AlCu. This leaves the use of electroless plating schemes to prepare MPW die for 2.5D/3D die stacking.

We propose a batch process to facilitate MPW die processing through the electroless under bump metallization (UBM) process. This process includes passivation of the Si die sidewalls post dicing, MPW die mounting, batch Zn or Sn immersion followed by electroless Ni, electroless Pd, immersion Au (ENEPIG) or electroless Ni, immersion Au (ENIG) UBM deposition for reliable, UBM deposition. We have demonstrated 2.5D integration of batch processed, AlCu finished die that have UBM deposited using this process to an interposer using electroplated Cu pillars bumps and Au bumps.

Supported by the Laboratory Directed Research and Development program at Sandia National Laboratories, a multimission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.

11:00am **MN+NS+PS-WeM10 MEMS-based Atomic Force Microscopy Probes: From Electromechanical to Optomechanical Vibrating Sensors**, *Bernard Legrand*, LAAS-CNRS, France; *L. Schwab*, LAAS-CNRS, Univ Toulouse, France; *P. Allain, I. Favero*, MPQ, CNRS, Univ Paris Diderot, France; *M. Faucher, D. Théron*, IEMN, CNRS, Univ Lille, France; *B. Walter*, Vmicro SAS, France; *J.P. Salvetat*, CRPP, CNRS, Univ Bordeaux, France; *S. Hentz, G. Jourdan*, CEA-LETI, France

INVITED

Scanning probe microscopy has been one of the most important instrumental discoveries during the last quarter of the last century. In particular, atomic force microscopy (AFM) is a cross-disciplinary technique able to provide sample morphology down to the atomic scale. It offers invaluable tools to support the development of nano-sciences, information technologies, micro-nanotechnologies and nano-biology. For more than 20 years, boosting the scan rate of AFM has been an increasingly important challenge of the community. However still today, performing routine and user-friendly AFM experiments at video rate remains unreachable in most cases. The conventional AFM probe based on a micro-sized vibrating cantilever is the major obstacle in terms of bandwidth and resonance frequency.

Following a brief description of the context of the work, the talk will first describe the development of AFM probes based on MEMS devices that make use of ring-shaped microresonators vibrating above 10 MHz. A focus will be dedicated to the electrical detection scheme. Based on capacitive transduction and microwave reflectometry, it achieves a displacement resolution of  $10^{-15}$  m/VHz, allowing the measurement of the thermomechanical vibration of the MEMS AFM probes in air. Imaging capability obtained on DNA origamis samples at a frame rate greater than 1 image/s will be shown as well as investigation of block copolymer surfaces to elucidate the tip-surface interaction when vibration amplitudes are lower than 100 pm.

In the following, our recent research direction at the convergence of the fields of micro/nanosystems and VLSI optomechanics on silicon chips will be presented. Optomechanical resonators allow indeed overcoming the resolution limitation imposed by usual electromechanical transduction schemes. Here, we will introduce fully optically driven and sensed optomechanical AFM probes which resonance frequency is above 100 MHz and Brownian motion below  $10^{-16}$  m/VHz, paving the way for high-Speed

AFM operation with exquisite resolutions at sub-angstrom vibration amplitudes.

11:40am **MN+NS+PS-WeM12 Suppressing Secondary Grain Growth in  $\text{Sc}_{0.125}\text{Al}_{0.875}\text{N}$  Using a CMOS Compatible Electrode**, *Giovanni Esteves, M. Berg, M.D. Henry, B.A. Griffin, E.A. Douglas*, Sandia National Laboratories

The electromechanical response of AlN can be enhanced by doping Sc into AlN up to ~43%. Challenges arise in processing high Sc doped AlN films due to the presence of secondary grain growth. Templating  $\text{ScAl}_{1-x}\text{N}$  (ScAlN) from a platinum bottom electrode has shown immense success in yielding highly textured *c*-axis ScAlN without the presence of secondary grain growth. However, platinum is not complementary metal-oxide-semiconductor (CMOS) compatible which makes it unattractive to those in industry. There is a need for a new bottom electrode that suppresses secondary grain growth while maintaining CMOS compatibility. In this work,  $\text{Sc}_{0.125}\text{Al}_{0.875}\text{N}$  and AlN films were grown on various underlying CMOS compatible metal stacks. Optimal film microstructure and texture was obtained for films deposited on highly textured {111} AlCu<sub>0.05</sub> bottom metal. AlN and ScAlN thicknesses were 750 nm and 850 nm and showed rocking curves of 0.81° and 1.09°, respectively. Atomic force microscopy was used to determine the presence of secondary grain growth and film roughness. The success of this bottom metal stack is attributed to lattice matching and low surface roughness which allows for highly oriented *c*-axis textured AlN and ScAlN. This work presents a metal stack that allows for the creation of higher Sc-doped AlN films while maintaining a high-quality microstructure and texture. Therefore, allowing for commercialization of Sc-doped AlN technologies which are capable of higher electromechanical coupling coefficients than AlN devices.

*This work was supported by the Laboratory Directed Research and Development program at Sandia National Laboratories. Sandia National Laboratories is a multi-mission laboratory managed and operated by National Technology and Engineering Solutions of Sandia, LLC., a wholly owned subsidiary of Honeywell International, Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA-0003525. This paper describes objective technical results and analysis. Any subjective views or opinions that might be expressed in the paper do not necessarily represent the views of the U.S. Department of Energy or the United States Government.*

## Nanometer-scale Science and Technology Division Room 203A - Session NS+2D+AN+MN+MP+SE-WeM

### Micro, Nano and Opto Mechanics

**Moderators:** Robert Ilic, National Institute of Standards and Technology, Alokik Kanwal, NIST Center for Nanoscale Science and Technology

8:20am **NS+2D+AN+MN+MP+SE-WeM2 The Collective Behavior of Large Ensembles of Coupled MEMS Cantilevers with Varying Natural Frequencies**, *Christopher Wallin*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *N. Dick*, Tel Aviv University, Israel; *R. De Alba, D.A. Westly*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *S. Grutzik*, Sandia National Laboratories; *A.T. Zehnder, R.H. Rand*, Cornell University; *V.A. Aksyuk*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology; *S. Krylov*, Tel Aviv University, Israel; *B.R. Ilic*, National Institute of Standards and Technology, Center for Nanoscale Science and Technology

The collective behavior of nonlinear, coupled micro- and nano-electromechanical (M/NEMS) resonators has been shown to exhibit a host of nontrivial dynamics including abrupt pattern switching, multistability, hysteresis, intrinsically localized modes, and synchronization. Additionally, M/NEMS resonator arrays are extremely responsive to environmental perturbations making them excellent candidates for sensing applications when operated linearly. With our work, we investigate the collective dynamics of coplanar interdigitated arrays of prismatic microcantilevers operating in both the nonlinear and linear regimes.

Two opposing, partially interdigitated cantilever arrays with 100 cantilevers apiece were fabricated using a silicon-on-insulator wafer. The device consists of a unique geometry in which each array has cantilever lengths expanding linearly across the device in opposite directions giving a distribution of natural frequencies. The arrays were engineered to allow for large scale, nonlinear out-of-plane beam deflections through the removal of the entire silicon handle layer beneath the active array area.

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For sufficiently large drive amplitudes, the resonators begin oscillating via combination parametric resonance (CPR) across the entire array. The CPR driven oscillations occur across a broad frequency band. The tunable coupling between nearest-neighbor cantilevers through fringing electrostatic fields provides a mechanism to vary the CPR response. Due to the sizable deflections, the device's nonlinearities are apparent including hysteresis effects. Our experimental results are supported and expanded by the development of a reduced order model based on the Galerkin decomposition which generates the leading features of our data including the CPR band.

When operating in the linear regime, the natural modes of the array have localized characteristics whereby a limited number of beams oscillate at each of the natural mode frequencies. Operating the device at higher harmonics increases mode separation as the propagation bands stretch. The distinct resonant peak separation coupled with the spatially confined modal response make higher harmonic operation of tailored, variable length cantilever arrays well suited for a variety of resonant based sensing applications.

**8:40am NS+2D+AN+MN+MP+SE-WeM3 Piezoelectric Optomechanical Systems, Krishna Coimbatore Balram, University of Bristol, UK INVITED**  
Nanoscale optomechanical systems, which rely on the strong interactions between co-localised optical and mechanical modes in nanoscale cavities, have been explored for a wide variety of applications ranging from sensing to signal transduction [Aspelmeyer et al., Rev. Mod. Phys. (2014)]. In this talk, I will discuss piezoelectric optomechanical platforms for efficient signal transduction between the radio frequency (RF) and optical domain. We use GaAs as our model platform (Balram et al., Optica (2014), Nature Photonics (2016), Phys. Rev. Applied (2017)) and discuss some of the research opportunities and challenges in this field, especially as we move towards higher mechanical frequencies (> 10 GHz).

**9:20am NS+2D+AN+MN+MP+SE-WeM5 Absolute Deflection Measurements in a MEMS/NEMS Fabry-Perot Interferometry System, Roberto De Alba, C.B. Wallin, G. Holland, National Institute of Standards and Technology; S. Krylov, Tel Aviv University, Israel; B.R. Ilic, National Institute of Standards and Technology**  
Micro- and nano-electromechanical systems (MEMS/NEMS) are among the most sensitive devices for detection of ultra-weak forces, masses, and displacements. The small scale of these structures affords them very high frequencies (MHz to GHz), high quality factors, rich nonlinear phenomena, and many other beneficial traits that make them ideal as sensors and testbeds of fundamental physics. Fabry-Perot laser interferometry is a widespread and robust technique for probing MEMS/NEMS devices because it is non-invasive and provides exceptional motion sensitivity ( $\approx 1$  pm/Hz<sup>1/2</sup>) from DC to roughly 100 MHz. This technique utilizes the silicon substrate beneath the MEMS/NEMS device as a static reference mirror; doing so provides common-mode noise rejection in contrast to interferometers that use an external reference mirror. Furthermore, this technique is compatible with a wide range of MEMS/NEMS materials, from common insulators and conductors to graphene and other atomically-thin membranes.

Despite the many strengths of this experimental technique, it suffers from two main drawbacks. Firstly, the measured signal becomes highly nonlinear for device displacements larger than  $\lambda/4$ , where  $\lambda$  is the laser wavelength. Secondly, because the silicon backplane is immovable, there is no simple or established technique for calibrating device motion. As such, published results utilizing this setup typically report deflection in "arbitrary units." In this work, we focus on fully characterizing the nonlinear aspects of a MEMS/NEMS Fabry-Perot interferometer and developing a generalized approach to calibrate device motion based the wavelength of light. We will demonstrate how to quickly and accurately determine both static and dynamic MEMS/NEMS deflection by measuring reflected laser power in the time domain. We will further show how a single calibration (made in the large-amplitude regime) can be applied to subsequent measurements taken at lower amplitudes as well as to measurements taken in the frequency domain (e.g. by a lock-in amplifier). Lastly, we will demonstrate the capability of imaging the first three vibrational modes of a MEMS cantilever by using a scanning laser.

**9:40am NS+2D+AN+MN+MP+SE-WeM6 Silicon on Insulator Electrostatically Actuated Bistable Cantilevers for Resonant Displacement/Acceleration Sensing, O. Halevy, E. Benjamin, N. Krakover, Y. Kessler, Slava Krylov, Tel Aviv University, Israel**

Resonant accelerometers incorporating vibrating beams demonstrate higher sensitivity and better robustness when compared to their statically operated counterparts. Electrostatic softening of the beams electrostatically coupled to the proof mass allows to enhance sensitivity of the resonant accelerometers. The displacement of the proof mass affects the gap between the mass and the beam and results in the beam's frequency change, which is maximal in the vicinity of the critical limit points of the voltage-deflection curve. The use of the snap-through buckling for this purpose is attractive since it is fully reversible and does not involve contact. While double-clamped curved bistable beams designed to demonstrate snap-through behavior can serve as resonant acceleration sensors [1], they suffer from high sensitivity to temperature and residual stress.

In this work we report on a design and fabrication of an electrostatically actuated bistable resonant cantilever [2], which demonstrates low sensitivity to the temperature and to the residual stress. The concept is based on the tailoring of the actuating force in such a way that the beam in its initial "as fabricated" configuration is positioned in the vicinity of the critical point. This is achieved by designing the actuating electrodes to be significantly thicker than the beam. Our reduced order (RO) Galerkin and coupled finite elements (FE) models results show that the frequency to deflection sensitivity of the  $L = 150 \mu\text{m}$  long,  $h = 16 \mu\text{m}$  wide and  $d = 1 \mu\text{m}$  thick cantilever can reach 20 Hz/nm. This is equivalent to the frequency to acceleration sensitivity of 388 Hz/g, obtained for the case of a  $4 \text{mm} \times 4 \text{mm} \times 20 \mu\text{m}$  proof mass.

While the model results are promising, fabrication of the device incorporating the beams and the electrodes of the different thicknesses is challenging. We demonstrate fabrication of the  $50 \mu\text{m}$  thick electrodes and  $\approx 6 \mu\text{m}$  thick cantilevers from the same device layer of a Silicon on Insulator (SOI) wafer. Two-stage deep reactive ion etching (DRIE) process was used for an initial patterning of the electrodes and of the cantilever and for the thinning of the beams. We discuss the details of the fabrication process and preliminary experimental results.

[1] N. Krakover, B. R. Ilic and S. Krylov, "Displacement Sensing Based on Resonant Frequency Monitoring of Electrostatically Actuated Curved Micro Beams," *J. Micromech. Microeng.*, **26**, pap. 115006, 2016.

[2] N. Krakover, S. Krylov, "Bistable Cantilevers Actuated by Fringing Electrostatic Fields," *ASME Journal of Vibration and Acoustics*, **139**(4), 040908-040908-10, 2017.

**11:00am NS+2D+AN+MN+MP+SE-WeM10 Electron-Photon-Phonon Hybrid Systems Based on Compound Semiconductor Mechanical Resonators, Hiroshi Yamaguchi, NTT Basic Research Laboratories, Nippon Telegraph and Telephone Corporation, Japan INVITED**

The use of compound semiconductor heterostructures as the elastic materials in the fabrication of micro/nanomechanical resonators has advantages, such like the improvement of mechanical properties through strain engineering, optomechanical transduction through carrier-mediated coupling, and piezoelectrically controllable nonlinearity [1]. The hybrid properties play the essential role in the operation where the different excitations of phonons, photons, and electrons are mutually interacted. In this invited talk, I will review our recent activities studying the electronic [2], photonic [3], and phononic [4] functions in GaAs-based mechanical resonators.

[1] H. Yamaguchi, *Semicond. Sci. Technol.* **32**, 103003 (2017).

[2] Y. Okazaki, I. Mahboob, K. Onomitsu, S. Sasaki, and H. Yamaguchi, *Nature Commun.* **7**, 11132 (2016).

[3] H. Okamoto, T. Watanabe, R. Ohta, K. Onomitsu, H. Gotoh, T. Sogawa, and H. Yamaguchi, *Nature Commun.* **6**, 8478 (2015).

[4] M. Kurosu, D. Hatanaka, K. Onomitsu, and H. Yamaguchi, *Nature Commun.* **9**, 1331 (2018).

**11:40am NS+2D+AN+MN+MP+SE-WeM12 Size Dependent Mechanics of Elastomers, Le Li, N. Alsharif, K.A. Brown, Boston University**

Elastomers are fascinating materials owing to the fact that their mechanical properties are dictated by entropy. Due to their low modulus, chemical compatibility, and ease of processing, they are widely applied in fields from soft lithography to medical devices. While it is well accepted that they exhibit fascinating size-dependent mechanical properties when confined to



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thin films, the structure-property relationships that govern confined elastomers are difficult to unambiguously determine due to the mechanical influence of rigid support structures and unavoidable contributions from adhesion. As a result, a consensus regarding the moduli of elastomeric thin films has not emerged. Here, we present a combined computational and experimental approach to measure the true mechanical properties of thin elastomer films. First, we utilize extensive finite element simulations to determine a correction to the Hertzian contact model that depends upon a dimensionless film thickness and the polymer Poisson's ratio. In order to verify this correction, films composed of three different thermoplastics were studied using an atomic force microscopy (AFM) nanoindenting. Interestingly, all three were observed to soften when confined to films thinner than 100 nm, in agreement with literature reports of buckling experiments. To explore softer elastomeric materials that exhibit categorically different behavior, we extended this correction to the Johnson-Kendall-Roberts (JKR) model that considers adhesion in contact mechanics. Elastomer thin films with different crosslink densities were studied using AFM nanoindentation and finite element simulation to determine their moduli. We observed a drastic stiffening on all elastomeric films when they were confined to sub-micrometer thicknesses. More importantly, modulus of all sub-100 nm elastomer films converges to the same trend regardless of bulk crosslink density. We present a hypothesized molecular model explaining this behavior. These results shed new light on the nanomechanics of elastomers and provide a general process for exploring size-dependent mechanics in polymers.

## Plasma Science and Technology Division

### Room 104C - Session PS+MN-WeM

#### IoT Session: Enabling IoT Era

**Moderators:** Ankur Agarwal, KLA-Tencor, David Lishan, Plasma-Therm LLC

#### 8:00am PS+MN-WeM1 A "Moore's Law" for Packaging, *Subramanian Iyer*, University of California at Los Angeles **INVITED**

While Silicon has scaled aggressively by over a factor of a few thousand over the last six decades the progress in packaging has been more modest – a linear factor 4-5 in most cases. In this talk, we will examine the reasons for this lag and what we are doing to fix this imbalance. Packaging is undergoing a renaissance where chip-to-chip interconnects can approach the densities of on-chip interconnects. We will discuss the technologies that are making this happen and how these can change our thinking on architecture and future manufacturing. Specifically, we will discuss two embodiments: Silicon as the next generation packaging substrate, and Flexible electronics using fan-out wafer level processing. We will describe how this is needed for the IoT era.

#### 8:40am PS+MN-WeM3 Fabrication, Chemical Lift-Off and Optical Characterization of Nanoscale III-Nitride Light Emitters, *Lesley Chan<sup>1</sup>, C.D. Pynn, P. Shapurenka, T. Margalith, S.P. DenBaars, M.J. Gordon*, University of California at Santa Barbara

High density, near eye, and flexible display technologies of the future will require efficient micro- and nanoscale pixels based on light emitting diodes (LEDs). Liquid-crystal displays (LCD) and organic LEDs are currently used or envisioned for these applications, but their efficiencies and lifetimes are low. Higher efficiency III-nitride materials are promising for such displays, but manufacturing and implementing sub-micron scale InGaN/GaN structures that emit at different wavelengths into devices is currently difficult. Moreover, flexible and curved display applications require substrate thinning or separating individual devices from their growth substrates for subsequent printing or pick-and-place onto alternate substrates.

In this talk, we present an easy and scalable fabrication and chemical lift-off method to create nanoscale InGaN LEDs, along with morphological and optical characterization of the resulting structures using photo- (PL) and cathodoluminescence (CL). Active and sacrificial multi-quantum well (MQW) layers were epitaxially grown on semipolar (20-21) GaN substrates using MOCVD and patterned into large mesas (4x4 mm<sup>2</sup>) using photolithography and Cl<sub>2</sub>/N<sub>2</sub> plasma etching. Mesas were 'flip-chip' bonded to sapphire and chemically released from the GaN growth substrate by photoelectrochemical (PEC) etching of the sacrificial MQW layer, leaving behind a 1-2 μm thick p-GaN/MQW/n-GaN device layer protected with Si<sub>3</sub>N<sub>4</sub>. Nano-LEDs (nLEDs) were then patterned on the thin film device layer

using colloidal lithography and plasma etching, released using HF vapor, and suspended in water, resulting in a colloidal solution of InGaN nLEDs. LED geometry was tuned by adjusting the SiO<sub>2</sub> colloid mask size (500-2000 nm) and plasma processing, e.g., using an isotropic CF<sub>4</sub>/Ar mask reduction etch and vertical GaN etch with Cl<sub>2</sub>/N<sub>2</sub>. Preliminary PL results show a five-fold increase in emission for on-wafer nLEDs compared to their planar (unpatterned) counterparts. The large PL enhancement is thought to be due to increases in both IQE and EQE resulting from relaxed strain (decreasing the quantum confined Stark effect) and enhanced light extraction from increased scattering and graded index effects (i.e., non-planar geometries), respectively. CL spectroscopy and imaging of individual nLEDs also revealed strong MQW emission after processing with peak wavelengths at 430 nm. This work suggests that the 'flip-chip' approach, combined with colloidal lithography and chemical release, is a viable route to solution processable, high efficiency nanoscale light emitters.

#### 9:00am PS+MN-WeM4 High Radical Flux, with Low Ion and Photon Flux, Plasma Source, for MEM'S Technology, *Marc Segers, Y. Pilloux, D. Lishan, S. FERRAND*, Plasma-Therm LLC

Micro-electromechanical system (MEMS) are main constituent of a variety of sensors, that include pressure and vibration sensors, accelerometers and gyroscopes, and radiation and temperature sensors. MEMS is a technology that could answer the IoT's requirements for sensors high sensitivity.

To be able to produce MEMS with lower cost and higher quality, different steps are necessary with preventive treatment, like substrate cleaning or sacrificial photoresist removal, with plasma.

In this work, we introduce a unique inductively coupled downstream plasma source configuration to generate high density radical concentration, for a chemical action and surface activation, but without high ion and photon fluxes, in opposition with conventional inductively coupled plasmas.

Our plasma technology provides a unique process capability for ultimate surface preparation, removal of most difficult residues formed during semiconductor and MEMS processing. System features an innovative approach to "Inductive Coupling", introducing a proprietary plasma confinement technology that is capable of a quasi-full gas dissociation inside the discharge tube, at low RF power. Although the plasma discharge tubes are isolated from the treatment chamber, with a remote plasma design, they deliver a large concentration of free radicals. That "High Density Radical Flux" technology (HDRF<sup>®</sup>) has demonstrated concentration levels up to 1,000 times higher than conventional plasma sources. HDRF<sup>®</sup> provides a damage free processing, allowing cleaning of high aspect ratio structures, preventing collapsing or stiction free of membranes, and activation of ultra-sensitive materials, that could be found in MEMS technology. Most of applications include Bosch polymer removal, low temperature photoresist stripping, descum and activation of ultrasensitive surfaces prior to bonding, like MEMS capsuling or shielding.

The low ion and photon exposure significantly reduces the opportunity for damage to sensitive layers. This inductive plasma arrangement prevents local heating and charging on the wafer. With that low local electrical potential, the HDRF<sup>®</sup> is efficient with 3D structures on the wafer (e.g. MEMS and other high AR features) where preventing ion shielding effects is important.

This work will first describe the HDRF<sup>®</sup> source and different advantages for MEMS processing. Second, several applications using the HDRF<sup>®</sup> technology will be discussed. These applications will include cleaning of 30:1 aspect ratio (AR) silicon vias, removal of sacrificial layers in MEMS structures, low temperature photoresist removal, and surface smoothing of Bosch generated sidewalls using micro-isotropic etching.

#### 9:20am PS+MN-WeM5 Use of Plasma in Advanced Packaging, *Michael Seddon*, ON Semi **INVITED**

Advanced Packaging is critical for the continually evolving demands of IoT. As additional functionality is added to the final product, and as its form factor is reduced to further promote mobility and compatibility, the semiconductor package has become even more critical in the integration and overall success of the technology. Advanced IoT packaging is required to offer not only the reliability and protection required of the technology, but it needs to offer the solution with the lowest possible power usage, most efficient use of space and footprint, improved thermal performance, while at a low cost to the end customer. This presentation will discuss several uses of plasma in advanced packaging solutions to meet these demands in both improving the overall reliability performance as well as offering new technology solutions.

<sup>1</sup> Coburn & Winters Student Award Finalist

# Wednesday Morning, October 24, 2018

## 11:00am PS+MN-WeM10 Low Temperature Plasmas in Nanotechnology Applications, *Meyya Meyyappan*, NASA Ames Research Center **INVITED**

The versatility and low temperature processing capability has allowed the use of gas discharges in a variety of nanotechnology applications. This talk will provide an overview of our activities on the use of low temperature plasmas in printed electronics and also the growth of nanomaterials and application development. We have developed an atmospheric pressure plasma jet as an alternative to inkjet and aerosol printing to deposit nanomaterials on paper, plastic, metal foils and textiles etc. to enable flexible, printable electronics. This is a single-step process that does not require a follow-on annealing or sintering in order to get consolidated thin films as is customary with other techniques. The surface temperature is in the range of 20-80 deg C depending on the carrier gas used and the morphology of the film can be controlled by varying the carrier gas and other plasma parameters. Examples of printed materials and their applications will be discussed. The talk will also cover growth of vertical graphene or carbon nanowalls using PECVD on various substrates with interesting properties as well as carbon nanofibers for a variety of applications. The author thanks Ram Gandhiraman, Jessica Koehne, Mike Oye, Mehrdad Shaygan, Mark Rummeli and Jeong-soo Lee.

## 11:40am PS+MN-WeM12 Gas Phase Synthesis of Pure III-V Semiconductor Nanoparticles from Bulk Metals by using Low Temperature Plasma, *Necip Berker Uner*, *E. Thimsen*, Washington University in St. Louis

III-V semiconductors are an important class of optoelectronic materials with applications that cover a broad range of the spectrum. Nanoparticles of many of the III-V materials, such as GaAs, InP and InSb, have been synthesized successfully with colloidal methods. However, high quality colloidal syntheses of stibnide and nitride nanoparticles haven't been reported yet. In this work, we present a general gas phase synthesis route for pure nanocrystals of GaSb and GaN. The method relies on reacting aerosols of different metals with help of a low temperature plasma (LTP). Aerosols of Ga, Sb and gaseous nitrogen bearing species were used as precursors. First, the aerosols of the constituent metals were generated via evaporation and condensation. Then, these aerosols were sent into a tubular argon LTP reactor, which provides continuous in-flight processing. As demonstrated in a previous study [1], particles vaporize in the LTP, and the resulting vapor may lead to nucleation of new particles or to re-condensation on the remaining clusters. During the synthesis of the III-V nanomaterials, unipolar charging prevents agglomeration, therefore free-standing particles were produced. Synthesized particles were found to be crystalline and they were mixed on an atomic scale. The stoichiometry was adjusted by manipulating input aerosol concentrations and applied plasma power. Materials were characterized *ex-situ* via high resolution transmission electron microscopy, energy dispersive x-ray spectroscopy, electron-energy-loss spectroscopy, x-ray diffraction and inductively-coupled plasma optical emission spectroscopy. The presentation will provide the results obtained through the extensive characterization methods mentioned. Furthermore, capping the synthesized particles with surfactants, effects of post-etching on the material, and photoluminescent properties will be presented. Operation of the aerosol sources and the mechanism leading to the formation of the compound materials will also be discussed.

[1] N. B. Uner and E. Thimsen, "In-Flight Size Focusing of Aerosols by a Low Temperature Plasma," *J. Phys. Chem. C*, vol. 121, no. 23, pp. 12936–12944, Jun. 2017.

## 12:00pm PS+MN-WeM13 Investigation of Fundamental Hydrocarbon Plasma Chemistry for Unraveling Film Deposition Processes on Nanomaterials, *Tara Van Surksun*, *E.R. Fisher*, Colorado State University

Nanostructured materials have numerous desirable properties (e.g., electronic, optical, high surface area) making them useful for range of applications (e.g., catalysts, sensors). However, in some cases, mechanical properties of the materials are not well-suited for their intended environment. Plasma processing of nanomaterials presents an ideal route to modify bulk and surface properties and ultimately, fine tune these materials for desired applications. Hydrocarbon plasmas are often employed to deposit amorphous hydrocarbon films and have been utilized in conjunction with nanostructured materials to increase material hardness. To date, however, a lack of understanding of the fundamental interactions between the material and gas-phase hinders material development. Thus, we aim to elucidate how hydrocarbon plasma deposition processes are influenced by substrate morphology and chemistry, and conversely, how the material ultimately influences the gas-phase chemistry of the plasma.

Here, inductively-coupled hydrocarbon plasma systems (e.g., CH<sub>4</sub>, C<sub>2</sub>H<sub>4</sub>) are investigated to elucidate the roles of gas-phase radicals and gas-surface interactions during film growth processes for flat (e.g., glass slides, Si wafers) and nanostructured (e.g., SnO<sub>2</sub>, TiO<sub>2</sub>, ZnO) substrates. Materials properties are also assessed to determine the influence of the plasma parameters on film quality. X-ray photoelectron spectroscopy confirms the deposition of amorphous hydrocarbon films on all substrates and scanning electron microscopy images show morphological differences between films deposited under different plasma conditions. Raman spectroscopy reveals that plasma processing creates oxygen vacancies in the TiO<sub>2</sub> lattice structure. Additionally, optical emission spectroscopy is utilized to determine relative species' densities and rotational and vibrational temperatures ( $T_R$  and  $T_V$ , respectively) for multiple species (e.g., CH, C<sub>2</sub>). In CH<sub>4</sub> plasma systems,  $T_V(\text{CH})$  ranges from ~2000 to ~4000 K under most plasma conditions, whereas  $T_R(\text{CH})$  generally reaches values ranging from 1800 to 2800 K. Both values appear to correlate with system pressure and applied rf power. In some cases, the nanostructured substrates have a measurable effect on the gas-phase chemistry (e.g., presence of additional gas-phase species, elevated  $T_R(\text{CH})$ ), whereas in others, the substrate does not appreciably alter the gas-phase of the plasma. Collectively, these data help to unravel these complicated systems by providing valuable insight regarding possible mechanistic phenomena in hydrocarbon plasmas linked to film deposition on materials with complex architectures.

## 2D Materials Focus Topic

Room 201B - Session 2D+MN+NS+SS-WeA

### IoT Session: Surface Chemistry, Functionalization, Bio and Sensor Applications

**Moderator:** Daniel Walkup, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park

2:20pm **2D+MN+NS+SS-WeA1 Impact of Hydrogen on Graphene-based Materials: Atomistic Modeling and Simulation of HRSTEM Images**, C. Guedj, Univ. Grenoble Alpes, CEA, LETI, France; L. Jaillet, F. Rousse, Stéphane Redon, Univ. Grenoble Alpes, CNRS, INRIA, Grenoble INP\*, IJK, France

The hydrogen energy transition is highly probable, because hydrogen is the most abundant element in the universe and represents an ideal “green” source of energy. Meanwhile, the safe hydrogen production and storage remains a major challenge still in progress. Potential production and storage materials include graphene. In terms of electronic and optoelectronic applications, hydrogen can tune the bandgap of graphene [1]. Hydrogen also plays a major role during the Chemical Vapour Decomposition (CVD) growth of graphene [2]. Hence, hydrogenated graphene-based materials are potentially relevant for various technological applications.

To understand and optimize the device efficiency and the interface engineering, it is advantageous to perform advanced nanocharacterizations, linked to numerical modelling and simulations. This task is particularly difficult, because hydrogen is labile and prone to rapid reorganization. This structural evolution may be monitored with transmission electron microscopy (TEM) techniques [3,4,5], but in spite of significant progresses, the direct detection of hydrogen with High Resolution Scanning Transmission Electron Microscopy (HRSTEM) or energy-loss spectroscopy still remains a serious challenge.

We investigate here the interaction of hydrogen with graphene using the Brenner module of the SAMSON software platform <https://www.samson-connect.net> and we propose an original methodology to characterize its structural arrangement at the atomic scale by simulating HRSTEM images to interpret experimental results. In particular, we compare the effect of hydrogen on dark field (DF), bright field (BF), high-angle annular dark field (HAADF) and annular bright field (ABF) images, to estimate the best technique suited to hydrogen detection.

In addition, we present the effect of carbon vacancies and adatoms on the stability of hydrogen coverage, associated to the HRSTEM signatures of the most stable configurations. These results provide the necessary building blocks to analyze the structure and energetics of hydrogenated graphene-based materials at the atomic scale.

#### References

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2:40pm **2D+MN+NS+SS-WeA2 High Density H<sub>2</sub> and He Plasmas: Can They be used to Treat Graphene?**, Hasan-Al Mehedi, Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France; D. Ferrah, Cea, Leti, Minatec, France; J. Dubois, C. Petit-Etienne, Laboratoire des Technologies de la Microélectronique, CNRS-UJF; H. Okuno, Cea, Inac/sp2m/lemma; V. Bouchiat, Institut Néel, CNRS-UJF-INP; O.J. Renault, CEA/LETI-University Grenoble Alpes, France; G. Cunge, Laboratoire des Technologies de la Microélectronique, CNRS-UJF, France

Since graphene and other 2D materials have no bulk, a major issue is their sensitivity to surface contaminations, and the development of cleaning processes is mandatory. High density plasmas are attractive to treat (clean, dope, pattern) 2D materials because they are a mature industrial technology adapted to large area wafer. However, in these plasmas the substrate is bombarded by a high flux of both thermal radicals and reactive ions with typical energy above 10 eV, which can easily damage atomic layer thin materials. We have investigated systematically the interaction of H<sub>2</sub> and He inductively coupled plasmas (ICP) with graphene in industrial reactors. We report a specific issue associated with the use of H<sub>2</sub> plasma: they etch the inner part of plasma reactor walls, thus releasing impurities in the plasma, most notably O atoms that etch graphene and Si atoms which stick on it. The presence of parasitic oxygen presumably explains the

discrepancies found in the literature regarding the impact of reactive plasmas on graphene damages. To get rid of this issue we propose to use a fluorinated aluminum chamber. In this case, fluorine atoms which are shown to be harmless to graphene are the only impurity in the plasma. Under such conditions H<sub>2</sub> ICP plasma is shown to clean graphene without damages if the ion energy is kept below about 15 eV.

3:00pm **2D+MN+NS+SS-WeA3 Novel Binder-free Ag@Ni(OH)<sub>2</sub> over Graphene/Ni Foam and Glucose Sensing**, Tong-Hyun Kang, J.-S. Yu, DGIST, Republic of Korea

Graphene combining with metal nanoparticles or other compounds is widely recognized to be a viable strategy to assemble high-activity catalysts. Unique properties of high conductivity and transparency, 2D morphology, and high stability in acid and alkaline solutions make graphene an excellent electron transfer medium on the interface of graphene/active materials as catalysts. Among them, graphene/metal nanoparticle (G/MNP) composites have been attracting more interest because of remarkably enhanced catalytic property, which is ascribed to a synergic effect from the interface of graphene and active sites. In general, reducing agents and electrodeposition methods have been employed to *in-situ* reduce metal ions such as Au<sup>3+</sup>, Pt<sup>4+</sup>, Ag<sup>+</sup>, and Cu<sup>2+</sup> (M<sup>n+</sup>) to MNPs on the graphene to form G/MNP composites. In this study, graphene is grown on nickel foam (NF) by chemical vapor deposition (CVD), which is directly used for MNP deposition. Different from bare NF, special phenomenon is observed that the graphene-coated nickel foam (GNF) composite can greatly speed up the electrodeless reduction of M<sup>n+</sup> ions on the surface of the graphene. Interestingly, the MNP deposition and Ni(OH)<sub>2</sub> nanosheet assembly simultaneously occur on the GNF. Binder-free Ni(OH)<sub>2</sub>-wrapped Ag hybrid developed on the GNF (Ag@Ni(OH)<sub>2</sub>-GNF) is found to serve as an efficient electrochemical sensor because of its unique structure. A low detection limit of 0.3 μM and high sensitivity are achieved for the glucose detection, which confirms that the hierarchical electrode structure of Ag@Ni(OH)<sub>2</sub>-GNF composite is highly effective to have extensive applications.

3:20pm **2D+MN+NS+SS-WeA4 Surface Modification and Magnetization of Carbon Based Nanostructures**, Rina Tannenbaum, University of Stony Brook; I.T. Kim, Gachon University, Korea; S. Sharma, University of Stony Brook

We describe here a novel synthesis for the facile decoration of carbon nanomaterials (CNM) with monodisperse γ-Fe<sub>2</sub>O<sub>3</sub> magnetic nanoparticles. These procedures were developed for multi-walled carbon nanotubes (MWNTs), reduce graphene (rGO) and reduced graphene nanoroses (rGO-roses). The decoration of these carbon nanomaterials with γ-Fe<sub>2</sub>O<sub>3</sub> induces the magnetization of these structures and opens up the potential for their use in novel applications.

CNM/γ-Fe<sub>2</sub>O<sub>3</sub> magnetic nanostructures were fabricated through a modified sol-gel process using ferric nitrate nonahydrate, Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O as a starting material. Nucleation sites for the iron oxide were generated at the CNM surface due to the electrostatic interaction between Fe (III) ions and the carboxylate surface groups of acid-treated CNMs. The occurrence of gelation was inhibited by the addition of the NaDDBS surfactant, before the addition of propylene oxide, which is a gel promoter. The surfactant interfered in the growth stage of the iron oxide nanoparticles (gel phase) through to the coordination of the NaDDBS molecules to the iron (III) centers due to the attraction between the negatively-charged hydrophilic head of the surfactant and the positively-charged iron. The rGO-roses were further fabricated from decorated rGO via a novel emulsion process.

Various characterization methods were used to confirm the formation of well-defined maghemite nanoparticles, and show that they were tethered to the walls of the CNMs. The tethered γ-Fe<sub>2</sub>O<sub>3</sub> nanoparticles imparted magnetic characteristics to the CNMs, which in turn, became superparamagnetic. The magnetic carbon nanotubes and magnetic rGO were introduced into a polymer matrix [¶] and were oriented parallel to the direction of an externally-applied magnetic field. The anisotropic nanocomposites were then used as anodes in lithium ion batteries. The magnetic rGO-roses were used as nuclear magnetic resonance contrast material.

# Wednesday Afternoon, October 24, 2018

4:20pm **2D+MN+NS+SS-WeA7 Chemical Modification of Graphene and Carbon Nano Tubes as viewed by XPS and NEXAFS Spectroscopies underpinned by DFT Spectra Simulation**, C. Ehlert, E. Donskyi, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany; P.L. Girard-Lauriault, McGill University, Canada; R. Illgen, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany; A. Lippitz, Bundesanstalt für Materialforschung und -prüfung (BAM); R. Haag, M. Adeli, Freie Universität Berlin, Germany; **Wolfgang Unger**, Bundesanstalt für Materialforschung und -prüfung (BAM), Germany

Graphene is a two-dimensional carbon network with unique properties. However, its low solubility, poor reactivity and the limited accessibility of a well-defined basal plane are major challenges for applications. An ideal method to overcome these problems is the covalent attachment of functional molecules to its surface which enable further reactive modifications for specific applications. There are several technologies for surface functionalization of graphene and related CNT materials. To get control on the functionalization process and to optimize the performance of the modified surfaces analytical tools for surface chemical characterization are required. X-ray absorption (NEXAFS) and photoelectron spectroscopy (XPS) have been identified to be rather powerful here [1-3]. Specifically, NEXAFS spectroscopy underpinned by quantum chemical spectrum simulations [4] is unique in a way to address changes of aromaticity and defect formation at the graphene surface during functionalization.

For relevant surface modification technologies, we present examples on how NEXAFS and XPS are fit for purpose. All presented modifications aim on the production of platforms for defined functional 2D nanomaterials, as for example multi-functional hybrid architectures. In detail we investigated:

- A wet chemical method for covalent functionalization of graphene sheets by a one-pot nitrene [2+1] cycloaddition reaction under mild conditions. Here a reaction between 2,4,6-trichloro-1,3,5-triazine and sodium azide with thermally reduced graphene oxide (TRGO) results in defined dichlorotriazine-functionalized graphene sheets.
- Graphene and carbon nanotube functionalized by Vacuum-Ultraviolet (VUV) induced photochemical or r.f. cw low pressure plasma processes to introduce amino, hydroxy or brominated functionalities.

To underpin finger-print information delivered by C K-edge NEXAFS we studied the effects of selected point and line defects as well as chemical modifications for a single graphene layer model by density functional theory based spectrum simulations.

## Acknowledgement

We acknowledge support by the team at the BESSY II synchrotron radiation facility in Berlin, Germany, as well as Dr. A. Nefedov (Karlsruhe Institute of Technology, KIT) from the HE-SGM Collaborate Research Group.

## References

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4:40pm **2D+MN+NS+SS-WeA8 Elastic Spongy Graphene-Functionalized Silicon Anode with Excellent Cycle Stability in Li battery**, **Byong-June Lee**, J.-S. Yu, DGIST, Republic of Korea

Graphite plays a prominent role as a typical anode material in the lithium ion batteries (LIBs) because of its high lithiation-dilithiation reversibility and low voltage window. Unfortunately, the capacity is limited to 372 mAh g<sup>-1</sup> [1,2]. To search for materials with higher lithium storage capacity, a great number of investigations on metal oxides (or sulfides), Sn, P, and Si have been carried out in recent decades. Among these materials, silicon can make alloy with lithium in the form of Li<sub>22</sub>Si<sub>5</sub> to deliver a highest theoretical gravimetric capacity of ~4200 mAh g<sup>-1</sup>, and thus is considered to be one of the most promising anode materials for next generation LIB. It is worth mentioning that its quite low delithiation potential and high lithium storage capacity can provide a wide working voltage window and energy density, which enable promising potential application in electric vehicles. However, those advantages are seriously offset by a great challenge of large volume expansion during lithiation process and the resultant breakage of bulk silicon particles and solid electrolyte interface (SEI), which causes a serious

damage to the electrode structure and thus gives rise to a fast decay of the specific capacity [3].

In this work, novel 3D spongy grapheme (SG)-functionalized silicon is for the first time demonstrated by chemical vapor deposition for a LIB anode, which can overcome the common silicon anode issues such as poor conductivity and volume expansion of Si as well as transfer of Li ion towards the Si. The elastic feature of graphene has excellent function to self-adaptively buffer the volume variation during charge-discharge process. In particular, different from traditional graphene or carbon shells (core-shell and yolk-shell), the spongy 3D graphene networks provide much improved unique functions with excellent long-cycle stability and rate capability. The Si@SG electrode exhibits excellent cycling performance with high reversible specific capacity [4]. A superior 95% capacity retention is achieved after 510 cycles. All the electrochemical performances get benefits from the well-designed functional SG shells, where interconnected nano-graphene structure not only guarantees a high conductive network but also provides more free paths for excellent mass transfer in addition to self-adaptive buffering capability.

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5:00pm **2D+MN+NS+SS-WeA9 Electrical and Structural Changes of Multilayer WSe<sub>2</sub> Transistors: Atmospheric Gas Adsorption and Long Term Aging**, **Anna Hoffman**, M.G. Stanford, C. Zhng, University of Tennessee Knoxville; I. Ivanon, Oak Ridge National Laboratory; A.D. Oyedele, D.G. Mandrus, University of Tennessee Knoxville; L. Liang, B.G. Sumpter, K. Xiao, Oak Ridge National Laboratory; P.D. Rack, University of Tennessee Knoxville

Interest in transition metal dichalcogenides (TMDs) for opto-electronic applications has been growing recently due to their unique properties and layered structure. Surface science and DFT simulations have corroborated p-type doping and n-type suppression of O<sub>2</sub> and H<sub>2</sub>O adsorption in TMDs however, electrical characterization has not been fully investigated. This presentation will demonstrate the reversible suppression of n-type conduction in ambi-polar WSe<sub>2</sub> via water adsorption, which logically has a larger impact as the WSe<sub>2</sub> thickness decreases. Additionally, we observe a reversible and irreversible n-type suppression and p-type doping which we attribute to H<sub>2</sub>O adsorption and isoelectronic oxygen chemisorption, respectively, at chalcogen vacancies during long term aging in atmosphere over 6 weeks. Finally, controlled oxygen plasma exposure is utilized to oxidize and p-type dope WSe<sub>2</sub>. We will overview our device fabrication and electrical testing procedure, and transfer characteristics for our as-fabricated devices for various WSe<sub>2</sub> thicknesses in air and in vacuum will be illustrated. Long-term (6 week) electrical measurements in both air and vacuum are compared to the as-fabricated devices. Finally, complementary atomic force microscopy and Raman Spectroscopy are used to characterize the devices

5:20pm **2D+MN+NS+SS-WeA10 Ion Migration Studies in Exfoliated 2D Molybdenum Oxide via Ionic Liquid Gating for Neuromorphic Device Applications**, **Cheng Zhang**, P.R. Pudasaini, A.D. Oyedele, University of Tennessee Knoxville; A.V. Ilev, K. Xiao, T.Z. Ward, Oak Ridge National Laboratory; D.G. Mandrus, University of Tennessee Knoxville; O.S. Ovchinnikova, Oak Ridge National Laboratory; P.D. Rack, University of Tennessee Knoxville

The formation of an electric double layer in ionic liquid (IL) can electrostatically induce charge carriers and/or intercalate ions in and out of the lattice which can trigger a large change of the electronic, optical and magnetic properties of materials and even modify the crystal structure. We present a systematic study of ionic liquid gating of exfoliated 2D molybdenum trioxide (MoO<sub>3</sub>) devices and correlate the resultant electrical properties to the electrochemical doping via ion migration during the IL biasing process. A nearly nine orders of magnitude modulation of the MoO<sub>3</sub> conductivity is obtained for the two types of ionic liquids that are investigated. In addition, notably rapid on/off switching was realized through a lithium-containing ionic liquid whereas much slower modulation was induced via oxygen extraction/intercalation. Time-of-Flight Secondary Ion Mass Spectrometry confirms the Li intercalation. Results of short-pulse tests show the potential of these MoO<sub>3</sub> devices as neuromorphic computing elements due to their synaptic plasticity.

# Wednesday Afternoon, October 24, 2018

5:40pm **2D+MN+NS+SS-WeA11 Infrared Absorption of Nanometer-scale Thermally Reduced Graphene Oxide**, *Erin Cleveland, J. Nolde, G. Jernigan, E. Aijfer*, U.S. Naval Research Laboratory

Strong optical absorption is of fundamental importance to infrared (IR) sensors, and it has been well established that graphene is one of the strongest IR absorbing materials, with approximately 2.3% absorption in the IR and visible regions for a single layer. While reduced graphene oxide (RGO) may not have quite the same absorption strength as graphene on a layer-by-layer basis, we believe that by controllably reducing the oxygen concentration within the GO films we can increase the absorption of the RGO film to approach that of graphene. RGO films, unlike graphene, however, can be made arbitrarily thick, allowing for much higher absorbance in a single pass. Here we explore the use of GO films of varying thickness and UHV annealing temperature to achieve near 100% midwave IR absorbance in a quarter-wave reflection filter structure consisting of an RGO film on top of a  $\lambda/4$ -thick  $\text{SiO}_2$  layer deposited over a Ti/Pd mirror.

Graphene oxide (GO) is a two-dimensional network consisting of a graphene basal plane decorated with oxygen moieties in the forms of carbonyls, epoxies and hydroxyl groups resulting in variable number of  $sp^2$  and  $sp^3$  bonding geometries. Theory indicates that GO bandstructure and transport are strongly dependent on the ratio of the  $sp^2$  and  $sp^3$  bonding fractions, and therefore, by controllably removing specific oxygen groups, one can tune its electronic, optical, and chemical properties. While it is difficult to modify the oxygen concentration using wet chemical processing, e.g. using hydrazine, GO can be thermally reduced in  $\text{H}_2$ - $\text{N}_2$  forming gas with more precise control. However, this procedure, like chemical reduction promotes the occurrence of N and H impurities, as well as carbon vacancies within the graphene basal plane, significantly degrading the electronic quality of the film. Here, we use ultrahigh vacuum ( $<10^{-9}$  Torr) annealing to controllably reduce the oxygen concentration in GO films while introducing fewer defects. Not only does UHV annealing prevent the introduction of impurities, but after oxygen removal, dangling bonds tend to reform in hexagonal structure. UHV annealing also enables in-vacuo measurement by x-ray photoelectron spectroscopy (XPS) to precisely characterize the overall oxygen concentration and its distribution within alcohol, epoxy and carbonyl species. Following an 800°C UHV anneal for example, we find that the oxygen concentration is reduced to ~5%, and the layer spacing is equivalent to epitaxial graphene grown on the C-face of SiC.

6:00pm **2D+MN+NS+SS-WeA12 Dielectric Properties of Carbon Nanomembranes prepared from aromatic Self-Assembled Monolayers and their application in All-Carbon Capacitors**, *Xianghui Zhang, P. Penner, E. Marschewski*, Bielefeld University, Germany; *T. Weimann, P. Hinze*, Physikalisch-Technische Bundesanstalt, Braunschweig, Germany; *A. Götzhäuser*, Bielefeld University, Germany

Carbon nanomembranes (CNMs) are two-dimensional materials that are made by cross-linking self-assembled monolayers (SAMs) of aromatic molecules via low energy electron irradiation. Previous studies of the charge transport in molecular junction incorporating SAMs and CNMs of oligophenyl thiols has been carried out by using conical eutectic Gallium-Indium (EGaln) top-electrodes<sup>1</sup> and conductive probe atomic force microscopy (CP-AFM)<sup>2</sup>. Additional investigations of the dielectric properties of pristine SAMs and CNMs were performed by impedance spectroscopy on EGaln tunneling junctions. Here we demonstrate the fabrication and characterization of all-carbon capacitors (ACCs) composed of multilayer stacks of dielectric CNMs that are sandwiched between two types of carbon-based conducting electrodes: (1) trilayer graphene made by chemical vapor deposition and mechanical stacking; (2) pyrolyzed graphitic carbon (PGC) made by pyrolysis of cross-linked aromatic molecules. The junction area is defined by the width of electrode ribbons, ranging from 1 to 2500  $\mu\text{m}^2$ , and the separation between two electrodes is tuned by the number of CNM layers. The frequency response of nanocapacitors was measured with an LCR meter. A dielectric constant of 3.5 and a capacitance density of up to 0.5  $\mu\text{F}/\text{cm}^2$  were derived from the junction capacitance. A dielectric strength of 6.2 MV/cm was determined. These results show the potential of carbon nanomembranes to be used as dielectric components in next-generation environment-friendly carbon-based molecular electronic devices.

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**MEMS and NEMS Group**

**Room 202B - Session MN+2D+AN+NS-WeA**

**IoT Session: MEMS for IoT: Chemical and Biological Sensing**

**Moderators:** Robert Davis, Brigham Young University, Sushma Kotru, The University of Alabama

2:20pm **MN+2D+AN+NS-WeA1 BioMEMS for Eye Applications**, *Yu-Chong Tai*, California Institute of Technology **INVITED**

The field of Micro-Electro-Mechanical Systems (MEMS) has advanced tremendously for the last 20 years. Most noticeably, however, the field has mostly advanced in microsensors such as pressure sensors, accelerometers, gyros, microphones for cell phone and smart instrumentation applications. Looking forward though, in my opinion, one future direction of MEMS/NEMS is for micro biomedical devices. Among many possible biomedical applications, one challenging but promising branch is micro implants. Why micro implants? Body tissues (especially neurons), once severely damaged, do not repair or regenerate easily and often leave behind permanent debilitating deficits. Engineering implant technologies to interface intact tissues and/or to replace defective functions have continued to be the main solutions for many diseases. As our world is facing more severe aging population problems, significant growth in implant applications is foreseeable. As a matter of fact, there are already many existing commercially available implants such as pacemakers and cochlear implants, but they all have a lot to improve. For examples, cardiovascular implants like defibrillator and pacemakers are still bulky, mechanically rigid, power hungry, and functionally limited. The future implants should be even smaller, flexible, power efficient and more versatile so that they can be used at places not possible before. This talk will review the research of implants done at the Caltech MEMS lab. More specifically, this talk will focus on bioMEMS implant devices to treat eye diseases. Examples of devices will cover the four major ophthalmic diseases, i.e., cataract, glaucoma, age-related macular disease and diabetic retinopathy that make of close to 80% of world blindness. It is believed that BioMEMS can also have many other opportunities for other organs in our body too.

3:00pm **MN+2D+AN+NS-WeA3 Real-Time, Single Cell, Size Measurements using a Facile, Multimode Microwave Resonator**, *Selim Hanay, H. Aydogmus, A. Secme, H.S. Pisheh, M. Kelleci, U. Hatipoğlu*, Bilkent University, Turkey

In this study, a facile microwave sensor is designed and fabricated to detect transient cells one by one and extract their morphological and electrical properties in real time, without labeling. Multiple modes can be measured by multiplexing the electronic frequencies to obtain multiple analytic parameters at the same time. Our simple fabrication technique obviates the need to complex fabrication process.

A microwave sensor, in the form of a microstrip line resonator, is constructed by fixing copper tape at the back and the front side of a 1-mm thick glass slide. The backside is covered entirely with the tape to form a ground plane; on the front side, a copper tape was thinned within a few mm, extended across the slide and terminated with SMA feed through. On the front side, just below the copper tape, five capillary tubes are placed to transport the cells into the active sensing region. Microwave signals are transmitted through the two SMA ports at the end of the glass slide, perpendicular to the flow. The resonator is formed by electrically shorting the input/output ports. An initial characterization of the device is done by using spectrum analyzer so that its first and second order mode frequencies are obtained.

A digital phase-locked loops (PLL) measurement system with PI controller was constructed to track the resonance frequencies of the first two modes simultaneously in real-time. The PLL system tracks the two modes of the microstrip line resonator to sense the frequency shifts originating from the passage of the cells in the capillary.

As a proof of concept, initial PLL measurements were done with DI water. As water flows through the tube, frequency shifts around 100 kHz were observed in both modes. Later on, wildtype *Skbr3* breast cancer cells were flown through the same capillary. Frequency shifts in both modes were the responses of the resonator to the passage of the *Skbr3* cells beneath microstrip-line. The ratio between the first and second mode frequency shifts can be used to determine the location of each cell by two-mode theory. The analyzed data indicates almost a constant slope, verifying the positional response of the sensors. Moreover, the size distribution of the cells is cumulated around a contour line for constant size as expected.

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Earlier, we had detected single cells and distinguished different oncogenic cell lines using a PDMS based device. With this work, single-cell detection and sizing are accomplished with a device paradigm that does not require any lithography, metal deposition under vacuum or precise alignment of electrodes.

We acknowledge funding from European Research Council (ERC) Starting Grant (REM, 758769).

4:20pm **MN+2D+AN+NS-WeA7 Magnetic Microsystems for Communications, Rob Candler**, University of California at Los Angeles  
**INVITED**

We are witnessing a rapid expansion of embedded devices (IoT) that have a variety of functions but a common requirement, to communicate with one another. These devices will be connected on a scale previously unseen, and they will therefore require an approach to efficiently generate and receive electromagnetic waves in a small form factor. One such approach is to rethink the way electrically small antennas operate, shifting from a current-based antenna to a voltage-controlled multiferroic antenna. Multiferroics are material systems with coupled magnetic and electrical properties, and they offer a new route for the miniaturization of magnetic field-coupled devices. Multiferroic systems allow for the conversion of magnetic flux to a voltage (and vice versa) without the need of a wire loop, avoiding inefficiencies due to Ohmic loss. *In particular, strain-coupled heterostructures* of magnetostrictive and piezoelectric materials have received much attention, as they can offer magneto-electric coupling many orders of magnitudes higher than found in single-phase materials. A rapidly emerging research space in multiferroics is the development of miniature wireless devices, such as antennas and energy harvesters, taking advantage of the efficient flux-to-voltage conversion of multiferroics. In this talk, I will present work showing the impact of multiferroic coupling on the ferromagnetic resonance in GHz Bulk Acoustic Wave resonators, as well as investigations in frequency mixing from non-linear multiferroic effects. These results are all in support of our goal create a microscale multiferroic antenna that is orders of magnitude more efficient than its classical antenna counterpart.

Furthermore, continued miniaturization of existing and emerging components that use magnets (atomic clocks, quantum computing, magnetic memory) will increase their sensitivity to external magnetic fields as well as the crosstalk between components. To address this need, we are developing techniques for on-chip magnetic shielding using multiple layers of permalloy. We will present recent results showing microscale magnetic shields fabricated by electroplating multiple permalloy layers into molds, as well as milliscale shields that were conformally electroplated on 3D printed sheaths.

5:00pm **MN+2D+AN+NS-WeA9 MEMS-Based Resonant Sensors for IoT Applications, Oliver Brand, M. Kim, P. Getz**, Georgia Institute of Technology  
**INVITED**

The presentation discusses resonant microsensors, in which the measurand affects a characteristic of the resonance behavior of a resonant microstructure or a resonant circuit, such as its resonance frequency or quality factor. Resonant sensing is a very versatile sensing approach and can be adapted to a large variety of physical, chemical and biological measurands. Especially when using the resonance frequency as the sensing signal, high resolution is achievable since frequencies can be measured accurately. The presentation will highlight two possible implementations of resonant chemical sensors for Internet of Things (IoT) applications, a cantilever-based electromechanical resonator and a purely electrical L-C resonance circuit.

The first example is an electro-mechanical resonant chemical sensor based on a silicon hammerhead structure coated with a polymeric sensing film for the detection of volatile organic compounds. The presentation will highlight how proper selection of the resonance mode, in this case an in-plane vibration mode, and device geometry can improve device performance and how fast temperature modulations of the resonant sensors enable the observation of signal transients that contain additional analyte information. The sensors are fabricated using a CMOS-compatible bulk-micromachining process, have resonance frequencies between 400-800kHz and achieve sub-ppm limits of detection for select analytes.

The second example is a purely electrical resonant chemical sensor in form of a flexible and stretchable L-C (inductor-capacitor) sensor, which is battery free and can be wirelessly interrogated. To achieve stretchable sensor characteristics, the spiral inductor and interdigitated capacitor structures are formed by a liquid metal, eutectic gallium-indium (EGaIn). A subtractive reverse stamping technique is used to form the conducting

liquid metal lines with dimensions as small as 2 $\mu$ m inside PDMS microchannels and a 3D heterogeneous integration technique is applied to vertically stack and electrically interconnect the capacitor and inductor structure. Liquid and gaseous analytes change the capacitance and are detected by wirelessly measuring the resonance frequency of the L-C circuit around 143MHz.

5:40pm **MN+2D+AN+NS-WeA11 Etched Silicon Microcolumn For Tunable Thermal Gradient Gas Chromatography, Aaron Davis, P. Schnepf, P.S. Ng, R.R. Vanfleet, R.C. Davis, B.D. Jensen**, Brigham Young University

The connection of the digital and physical world will be strengthened by chemical sensors that can measure complex mixtures of molecules. Gas chromatography is the gold standard for identification of volatiles and gases. Conventional gas chromatography systems have unparalleled resolution, but are large and power intensive. Microcolumn gas chromatographs are more portable but have dramatically reduced resolution. Combining the resolution of conventional systems with the size factor of micro systems is important for improving the affordability and portability of high performance gas analysis. Recent work has demonstrated feasibility of high resolution separation of gases in a benchtop-scale short-column system by controlling thermal gradients through the column. In order to further decrease the size of a gas chromatography system, microfabrication techniques were used to demonstrate the fabrication of a thermally controllable micro-scale gas chromatographic column with a small footprint (3 cm square). To fabricate microcolumns we are using deep-reactive-ion-etching, nickel evaporation, and wafer bonding. The design of the 20 cm column utilizes 21 individually controllable thin film heaters and solid conduction cooling to produce the desired thermal profile.

## Nanometer-scale Science and Technology Division

### Room 203A - Session NS+MN+PC+SS-WeA

#### IoT Session: Bio at the Nanoscale

**Moderators:** Juraj Topolancik, Roche Sequencing Solutions, Liya Yu, NIST Center for Nanoscale Science and Technology

3:00pm **NS+MN+PC+SS-WeA3 Nanoscale Label-free Imaging of Protein Molecules via Photo-induced Force Microscopy, D. Nowak, Sung Park**, Molecular Vista

Nanoscale real space imaging of biological and biomaterial surface is not straightforward even with advances in microscopy techniques. Photo-induced Force Microscopy (PiFM) [1] combines infrared (IR) absorption spectroscopy and atomic force microscopy (AFM) via illumination of the tip-sample junction with tunable IR laser light and mechanical detection of forces acting on the tip in response to absorption of light by the sample. By mapping the IR absorption of the sample as a function of IR wavelength and position, nm-scale resolution is achieved in displaying the locations of heterogeneous materials on the surface of a sample. For protein molecules, amide I and II bands are readily accessible via tunable quantum cascade laser and provide ways to interrogate the molecule's local chemical environment. PiFM can provide both high resolution spectral imaging at a fixed wavenumber and full PiFM spectrum (analogue to FTIR spectrum) with a spectral resolution of 1  $\text{cm}^{-1}$  and spatial resolution of sub-10 nm. Results on collagen molecules, individual icosahedral protein cages, and nanoparticle/protein systems will be presented.

[1] D. Nowak et al., *Sci. Adv.* **2**, e150157 (2016).

3:20pm **NS+MN+PC+SS-WeA4 Evaluating Reaction-diffusion Immunoassays via High-resolution Imaging Techniques, Imanda Jayawardena**, University of Queensland, Australia; *S. Corrie*, Monash University, Australia; *L. Grondahl*, University of Queensland, Australia

Immunodiffusion is a simple assay used for the determination of a target protein concentration in a biological sample using a distance-based measurement. The assay allows the sample containing the antigen of interest to combine with an antiserum in a gel-based substrate leading to the formation of a ring-shaped precipitate ('precipitin ring'), the size of which is proportional to target protein concentration.<sup>1</sup> Using the malarial antigen HRP2 and antisera from immunized rabbits as the model system, for the first time, we are investigating transforming the current immunodiffusion assays into a more rapid and sensitive format.

The traditional assay substrate, agarose, is a severely diffusion limited system. The porosity of the gel is a key determinant of diffusion properties and is an essential parameter required for the study and modification of

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the assay. However, the scientific data on agarose pore size determination is based on artefact laden microscopy images of agarose hydrogels. Thus, we have performed an in-depth investigation on best imaging techniques for accurate pore size determination. The precipitin ring structure is a band of antigen-antibody precipitate, in significant contrast with the surrounding gel substrate. A brief preliminary investigation has been reported by Fedorov et al. on precipitin ring structure<sup>2</sup>, and we have extended this work by applying microscopic imaging techniques.

For imaging hydrogels, high pressure frozen gels were subjected to cryo-SEM<sup>3</sup>, and was established as the most accurate technique to study the native structure of the gel. Atomic force microscopy was found to complement cryo-SEM data while CLSM due to its limited resolution was found to be inadequate for the imaging of hydrogels. For imaging the protein-rich precipitin ring structure, high pressure frozen ring sections were subjected to cryo-SEM, however, more meaningful insight on the ring structure was obtained in this instance through CLSM studies.

Herein, we aim to present our work described above on imaging agarose hydrogels for accurate pore size determination and imaging precipitin ring structures associated with immunodiffusion assays.

1. Mancini, G.; Carbonara, A. t.; Heremans, J. *Immunochemistry* **1965**

2. Fedorov, A. A.; Kurochkin, V. E.; Martynov, A. I.; Petrov, R. V. *Journal of Theoretical Biology* **2010**

3. Aston, R.; Sewell, K.; Klein, T.; Lawrie, G.; Grøndahl, L. *European Polymer Journal* **2016**

4:20pm **NS+MN+PC+SS-WeA7 The Last Nanometer – Hydration Structure of DNA and Solid Surfaces Probed by Ultra-High Resolution AFM, Uri Sivan, K. Kuchuk, I. Schlesinger**, Technion - Israel Institute of Technology, Israel **INVITED**

Recent advancements in atomic force microscopy facilitate atomic-resolution three-dimensional mapping of hydration layers next to macromolecules and solid surfaces. These maps provide unprecedented information on the way water molecules organize and bind these objects. Since the hydration structure governs the energetics of solvation and interactions between objects immersed in solution, the new data are invaluable when trying to resolve fundamental questions such as identification of molecular binding sites and interaction mechanisms.

After a short presentation of our home-built microscope, characterized by sub 0.1 Å noise level, the talk will focus on two representative studies. The first one will disclose our recent finding that in solutions in contact with atmosphere, hydrophobic surfaces are generically coated with a dense layer of adsorbed gas molecules. This layer renders the hydrophobic interaction a certain universality, regardless of the underlying surface. The second study will present our recent success in obtaining ultra-high resolution images of DNA and 3d maps of its hydration structure. This study shows that labile water molecules concentrate along the DNA grooves, in agreement with known position of DNA binding sites.

5:00pm **NS+MN+PC+SS-WeA9 Open-hardware, High-speed Atomic Force Microscopy using Photothermal Off-resonance Tapping, Georg Fantner**, École Polytechnique Fédéral de Lausanne, Switzerland **INVITED**

Self-assembly of protein complexes is at the core of many fundamental biological processes. To reach a comprehensive understanding of the underlying protein self-assembly reactions, high spatial and temporal resolution must be attained. This is complicated by the need to not interfere with the reaction during the measurement. Since self-assemblies are often governed by weak interactions, they are especially difficult to monitor with high-speed atomic force microscopy due to the non-negligible tip-sample interaction forces involved in current methods. Here we develop a high-speed atomic force microscopy technique, photothermal off-resonance tapping (PORT), which is gentle enough to monitor self-assembly reactions driven by weak interactions. Using photothermal actuation on ultra-small HS-AFM cantilevers we perform force-distance curves at two orders of magnitude higher rates than in conventional off-resonance methods. From the time-domain tip sample interaction we extract tip-sample force curves to quantify the “static” forces due to the cantilever deflection, and the “impact” forces due to the rapid deceleration of the cantilever tip upon impact. Experimental characterization of the tip-sample forces in HS-tapping mode-AFM and PORT revealed that imaging forces in PORT are less than 1/5<sup>th</sup> of those exerted in conventional HS-AFM.

One of the key enabling factors for PORT is the real time control of the cantilever position using photothermal excitation. This requires low level, control of the feedback architecture and optimized AFM instrumentation. I will discuss the relevant components developed in my laboratory and explain how we share them with the broader scientific community using an open-hardware scheme.

We apply PORT to dissect the self-assembly reaction of SAS-6 proteins, which form a nine-fold radially symmetric ring-containing structure that seeds formation of the centriole organelle present in all eukaryotic cells. Using machine learning algorithms we traced hundreds of molecules over time to extract reaction kinetics from single molecule interactions. These measurements show that 9-fold closed SAS-6 rings are under pre-tension in their natural state. Due to the high temporal and force resolution provided by PORT, we found that, contrary to the current belief, more than one assembly route exists to reach the nine fold symmetry. These observation resets our current thinking about the assembly kinetics of this crucial step in cell replication.

5:40pm **NS+MN+PC+SS-WeA11 Development of Multimodal Chemical Nano-Imaging for *in situ* Investigations of Microbial Systems, A. Bhattarai, B.T. O'Callahan, P.Z. El Khoury, Scott Lea**, Pacific Northwest National Laboratory; K.-D. Park, E.A. Muller, M.B. Raschke, University of Colorado Boulder

Existing genomic and biochemical methods cannot directly probe the physical connections involved in microbial metabolic processes over relevant length scales, spanning the nano-meso-micrometer spatial regimes. Determining the location and function of such biomolecules would aid in identifying the mechanisms governing microbial interactions. We are addressing these technical and conceptual gaps by developing a single multimodal chemical imaging platform that can interrogate biomolecules in living systems using three complementary label-free, nanoscale, ultrasensitive chemical imaging techniques:

Infrared scattering scanning near-field optical microscopy (IR s-SNOM)

Tip-enhanced Raman nano-spectroscopy (TERS)

Multimodal hyperspectral optical nano-spectroscopy.

We have built and developed these imaging modalities independently prior to integration into a single, multimodal chemical nanoscope. As part of our benchmarking experiments, we performed TERS measurements targeting prototypical systems and constructs and demonstrated <1 nanometer precision in ambient TERS chemical imaging measurements.<sup>[1]</sup> We also established an overall broader scope of TERS<sup>[2]</sup> and illustrated that TERS is not restricted to nanoscale chemical imaging, but can also be used to probe different aspects of local fields confined to a few nanometers. Our new setup, equipped with a hyperspectral imager, enables hyperspectral fluorescence, optical absorption, dark-field scattering, Raman scattering, and topographic imaging. Recently, we used this capability to visualize pigments in lipid monolayers and within a single live *T. lutea* cell in solution.<sup>[3]</sup> For IR s-SNOM, we are working on developing an AFM capable of bottom illumination and collection of IR light to support measurements in aqueous environments. The approach would use a piezoelectric scanner mounted ZnSe prism to enable evanescent wave illumination and collection of scattered IR light. We are also benchmarking the IR s-SNOM with the TERS and hyperspectral imaging modalities on a number of model biological systems including bacteria, collagen, and cytochromes.

This unique AFM-based instrument could be used to investigate a wide range of biomolecules through their characteristic electronic and vibrational signatures, over the nano-meso-micrometer scales. This platform will not only enable recording chemical images of single microbial cells at the subcellular level, but it will also enable mapping entire microbial communities with chemical selectivity.

1. Bhattarai A and El-Khoury PZ (2017) *Chem Commun***53**(53): 7310-7313.

2. Bhattarai A et al. (2017) *Nano Lett***17**(11): 7131-7137.

3. Novikova IV et al. (2017) *Chem Phys***498-499**: 25-32.

## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MI+MN+NS+SS-ThM

### Novel 2D Materials

Moderator: Han Wang, University of Southern California

8:20am **2D+EM+MI+MN+NS+SS-ThM2 Controlled Growth of 2D Ni-Silicate and Silica Films on Ni<sub>x</sub>Pd<sub>1-x</sub> (111) Substrates**, *Chao Zhou, X. Liang, G.S. Hutchings, Z. Fishman, J.-H. Jhang, S. Hu, S. Ismail-Beigi, U.D. Schwarz, E.I. Altman*, Yale University

The discrete lattice constants and distinct chemical properties of different transition metal substrates hamper the systematic study of how the substrates can influence two-dimensional (2D) materials growth. The recent report of single-crystal epitaxial Ni-Pd alloy films with continuously tunable lattice constants open the possibilities to tackle this issue. Two-dimensional silica and transition-metal-doped silicate films prepared on metal substrates can be 2D analogues of porous bulk zeolites. In this research, 2D silica and Ni-silicate films were prepared on Ni<sub>x</sub>Pd<sub>1-x</sub> (111) substrates under different growth conditions. After annealing in 2×10<sup>-6</sup> Torr oxygen, Ni from the alloy substrates incorporates into the silica structure to form a crystalline 2D Ni-silicate structure, while an amorphous 2D silica bilayer can be observed after being annealed in 4×10<sup>-8</sup> Torr oxygen. Density functional theory (DFT) was employed to model various silica and silicate phases on Ni<sub>x</sub>Pd<sub>1-x</sub> (111) substrates. The results show that the 2D Ni-silicate films are thermodynamically stable on the substrates when the oxygen chemical potential is in the oxygen-rich range. In oxygen-deficient environments, 2D silica tends to form a stable Ni-free phase. With continuous control over the composition of NiPd alloy films, the surface strain applied on the Ni-silicate films through the lattice mismatch between the substrate and overlayer could also be continuously tuned. Only single-domain commensurate crystalline 2D Ni-silicate can be observed in zero or low-strain systems, while a second incommensurate crystalline domain which is rotated by 30° with respect to the commensurate domain can be observed when the lattice mismatch is over 1.85%.

8:40am **2D+EM+MI+MN+NS+SS-ThM3 Topological Materials**, *Hsin Lin*, Institute of Physics, Academia Sinica **INVITED**

Topological materials host various novel quantum phases of electrons which are characterized by band topology and topologically protected surface/edge states. Despite recent progress, intense world-wide research activity in search of new classes of topological materials is continuing unabated. This interest is driven by the need for materials with greater structural flexibility and tunability to enable viable applications in spintronics and quantum computing. We have used first-principles band theory computations to successfully predict many new classes of topologically interesting materials, including Bi<sub>2</sub>Se<sub>3</sub> series, the ternary half-Heusler compounds, TlBiSe<sub>2</sub> family, Li<sub>2</sub>AgSb-class, and GeBi<sub>2</sub>Te<sub>4</sub> family as well as topological crystalline insulator (TCI) SnTe family and Weyl semimetals TaAs, SrSi<sub>2</sub>, (Mo,W)Te<sub>2</sub>, Ta<sub>2</sub>S<sub>2</sub>, and LaAlGe family. I will also highlight our recent work on unconventional chiral fermions in RhSi and several material candidates for new TCI.

9:20am **2D+EM+MI+MN+NS+SS-ThM5 Few-Layer Rhenium Disulfide Synthesized Via Chemical Vapor Deposition**, *Michael Valentin*, Army Research Laboratory; *A. Guan, A.E. Nguyen, I. Lu, C.S. Merida, M.J. Gomez*, University of California, Riverside; *R.A. Burke, M. Dubey*, Army Research Laboratory; *L. Bartels*, University of California, Riverside

Transition metal dichalcogenides (TMDs) are exciting new materials that have received much attention due to their semiconducting properties in the direct bandgap. Well-studied TMDs, such as molybdenum disulfide (MoS<sub>2</sub>) and tungsten diselenide (WSe<sub>2</sub>), exhibit a direct bandgap in the monolayer form, but an indirect bandgap in the bulk form. Rhenium disulfide (ReS<sub>2</sub>), on the other hand, is a new TMD that is unique in its ability to retain a direct bandgap independent of thickness. By using chemical vapor deposition (CVD), few-layer ReS<sub>2</sub> is synthesized and characterized by optical methods such as Raman spectroscopy and photoluminescence. We also show characterization results for atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), scanning electron microscope (SEM), transmission electron microscope (TEM), and electrical transport to determine thickness, crystallinity, homogeneity, and electrical characteristics for use in future flexible electronics.

9:40am **2D+EM+MI+MN+NS+SS-ThM6 Dipolar Disorder of a van-der-Waals Surface Revealed by Direct Atomic Imaging**, *M.A. Susner*, Air Force Research Laboratory; *M.A. McGuire, Petro Maksymovych*, Oak Ridge National Laboratory

Recently, the family of transition metal thiophosphates –exhibiting ferroelectric, antiferromagnetic and correlated electron ground states – have gained attention as possible control dielectrics for the rapidly growing family of 2D and quasi-2D electronic materials [1]. Being van-der-Waals crystals, the surfaces of these materials can be created without dangling bonds, unlike those of complex oxides. Yet, because of robust insulating properties, the structure of their surfaces, the role of disorder, the structure of the topological defects in the order parameter and many other properties directly relevant to their prospective interfaces is almost entirely unknown.

Here we present the first atomically resolved imaging of CuScP<sub>2</sub>S<sub>6</sub> s carried out using cryogenic non-contact atomic force microscopy. The surface exhibits good crystalline ordering at the atomic scale, revealing contrast on sub-unit cell level. The most remarkable property is long-range commensurate modulation of the surface morphology, with a topographic amplitude of only 2-3 pm. Combined with XRD analysis of the bulk and Monte-Carlo simulation of the Ising model on triangular lattice, we propose that the modulation arises from antiferroelectric polarization domains, albeit with frustrated long-range order. The key structural ingredient for this state is centrosymmetric position of Sc<sup>3+</sup> within the layer, which forces the surrounding displacing Cu+1 ions to adopt a frustrated antiferroelectric state - in direct analogy frustrated magnetic systems. We will further discuss the peculiarities of nc-AFM imaging of this materials from the statistical analysis of the variation of images between scan, as well as the force-distance curve arrays. The possibility to directly visualize polar order opens broad opportunities to understand the atomistic aspect of ferroelectric, glassy and incommensurate phases in this material class, beginning with CuInP<sub>2</sub>S<sub>6</sub> – which exhibits Curie temperature ~315K and giant negative electrostriction [2]. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy. Microscopy experiments were conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

[1] Susner Michael A., Chyasnovichyus Marius, McGuire Michael A., Ganesh Panchapakesan, and Maksymovych Petro, *Advanced Materials* **29**, 1602852 (2017).

[2] S. M. Neumayer, E. A. Eliseev, M. A. Susner, A. Tselev, B. J. Rodriguez, S. Jesse, S. V. Kalinin, M. A. McGuire, A. N. Morozovska, P. Maksymovych, and N. Balke, *ArXiv:1803.08142 [Cond-Mat]* (2018).

11:00am **2D+EM+MI+MN+NS+SS-ThM10 Advanced ARPES Analyzer and Momentum Microscope KREIOS 150 – Concepts and first results on layered materials and topological insulators**, *Paul Dietrich, M. Wietstruck, T.U. Kampen, A. Thissen*, SPECS Surface Nano Analysis GmbH, Germany

Modern ARPES analyzers provide a high degree of parallelization in data acquisition, recording hundreds of energy and angle channels simultaneously. Additionally, integrated deflectors enable users to perform angle scanning perpendicular to the analyzer's entrance slit to record (k<sub>x</sub>, k<sub>y</sub>, E) data sets without sample rotation. However, the design of conventional analyzers implies a limited acceptance angle and corresponding accessible momentum space volume. Due to the trade-off between acceptance angle and angle resolution multiple changes in sample position and lens modes are necessary during a typical high resolution ARPES experiment. The new KREIOS 150 Energy Analyzer uses an extractor zoom lens design to overcome these limitations.

This new lens provides a full solid acceptance angle with highest angular resolution. In contrast to standard ARPES measurements with conventional hemispherical analyzers, electronic structure data from and beyond the 1<sup>st</sup> Brillouin zone is recorded without any sample movement. In addition the lens of such an instrument can work in a lateral imaging mode for microscopy as well. This enables navigation on the sample and reduces the size of the area under investigation in ARPES down to a few micrometers in diameter. This combination of large acceptance angle, high angular resolution and small acceptance area, makes this instrument the ideal tool for electronic structure studies on small samples or sample areas. The design is compact with a straight optical axis.

The capabilities of this instrument were tested at the UE 56/2 at the Bessy II synchrotron in Berlin. Specification tests show excellent angle and lateral resolution as well as small spot capability down to 2µm FOV. Subsequently



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real live samples like Graphene on Germanium were measured. Even on macroscopically rough surfaces like Graphene on NbSe<sub>2</sub> excellent ARPES and X-PEEM results could be obtained. By taking advantage of the small spot capability of the KREIOS 150 meaningful band structure data has been recorded on such patchy samples.

Acknowledgements: We thank Yu. Dedkov (University of Shanghai, China) and M. Foinin (University Konstanz) for providing beamtime and samples for the measurements with KREIOS 150 at BESSY II.

11:20am **2D+EM+MI+MN+NS+SS-ThM11 Carbon Nanomembranes with Sub-nanometer Channels: 2D Materials for Water Purification with High Selectivity and Highest Permeance**, Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X.H. Zhang, A. Beyer, S. Koch, D. Anselmetti, **Armin Götzhäuser**, Bielefeld University, Germany

Clean water is a global challenge, and membrane filtration is a key technology to achieve it. Here, we report on carbon nanomembranes (CNMs) with sub-nanometer channels that prove to be excellent water filters, combining a high selectivity with an exceptionally high water permeance. The CNMs are fabricated via the cross-linking of terphenyl self-assembled monolayers [1], resulting in a ~1.2 nm thick membrane perforated by channels with diameters below ~0.7 nm and areal densities of ~10<sup>18</sup>m<sup>-2</sup>. When tested as filter membranes, it was found that the CNMs efficiently block the passage of most gases and liquids [2]. However, water passes through, and it does this with a record-breaking permeance of ~1.1×10<sup>-4</sup> mol·m<sup>-2</sup>·s<sup>-1</sup>·Pa<sup>-1</sup>. This suggests that water molecules translocate fast and cooperatively through the sub-nanometer channels. Assuming all channels in a TPT-CNMs are active in mass transport, we find a single-channel permeation of ~66 water molecules·s<sup>-1</sup>·Pa<sup>-1</sup>. We compare this with molecular transport through other carbon nanoconduits, such as carbon nanotubes or membrane proteins (aquaporins). As the fabrication of CNMs is scalable, their utilization opens a path towards the application of 2D-materials in energy-efficient water purification.

[1] A. Turchanin and A. Götzhäuser: Carbon Nanomembranes, *Adv. Mater.* **2016**,28, 6075.

[2] Y. Yang, P. Dementyev, N. Biere, D. Emmrich, P. Stohmann, R. Korzetz, X. Zhang, A. Beyer, S. Koch, D. Anselmetti, A. Götzhäuser, *ACS Nano*, in press.

11:40am **2D+EM+MI+MN+NS+SS-ThM12 Discovery of Dirac Monolayers and Elucidation of Functonalites by Advanced Soft X-ray Spectroscopy**, **Iwao Matsuda**, University of Tokyo, Japan **INVITED**

Vapor deposition of three-dimensional (3-D) crystal on a substrate often results in formation of the novel 2-D materials with intriguing electronic states. The approach has been well-known in the field of "Surface Science", which has attracted our attentions over the past decades. Triggered by fabrication of the graphene layers, researches on such monatomic sheets have extended to various kinds such as silicene, germanene and so on. Soft X-ray spectroscopies, such as photoemission spectroscopy, have been used to directly probe electronic states of monatomic layers and also to examine carrier dynamics under the *operando* condition. We recently observed Dirac Fermions in a 2-D boron sheet, borophene, that forms spontaneously on the Ag(111) surface. Furthermore, we found pairing of the Dirac cones due to Moire-periodic perturbations of the overlayer-substrate interactions. In the Cu<sub>2</sub>Si monolayer, we also discovered the 2-D Dirac nodal line fermions that are protected by the mirror reflection symmetry. In the presentation, I will describe details of our research on the novel 2-D Dirac materials and introduce the advanced soft X-ray techniques that reveal their functionalities for developing devices.

[1] B. Feng, *IM et al.*, *Phys. Rev. Lett.*, **118**, 096401 (2017).

[2] B. Feng, *IM et al.*, *Adv. Mater.* **30**, 1704025 (2018).

[3] B. Feng, *IM et al.*, *Nature Comm.*, **8**, 1007 (2017).

## Electronic Materials and Photonics Division Room 101A - Session EM+MI+MN+NS-ThM

### Nanostructures for Electronic and Photonic Devices

**Moderators:** Sang M. Han, University of New Mexico, Jason Kawasaki, University of Wisconsin - Madison

8:00am **EM+MI+MN+NS-ThM1 Extreme Nanophotonics from Ultrathin Metallic Junctions**, **Maiken Mikkelsen**, Duke University **INVITED**  
New optical nanomaterials hold the potential for breakthroughs in a wide range of areas from ultrafast optoelectronics such as modulators, light sources and hyperspectral detectors, to efficient upconversion for energy

applications, bio-sensing and on-chip components for quantum information science; they also serve as inspiration for entirely new devices and technologies. An exciting opportunity to realize such new nanomaterials lies in controlling the local electromagnetic environment on the atomic- and molecular-scale, (~1-10 nm) which enables extreme field enhancements, but represents a largely unexplored length scale. We use creative nanofabrication techniques at the interface between chemistry and physics to realize this new regime, together with advanced, ultrafast optical techniques to probe the emerging phenomena. Here, I will provide an overview of our recent research demonstrating tailored light-matter interactions by leveraging ultra-small plasmonic cavities fabricated using bottom-up techniques. Examples of our demonstrations include perfect absorbers and combinational colors [*Adv. Mat.* **27**, 7897 (2015), *Adv. Mat.* **29**, 1602971 (2017)], actively tunable nanostructures [*Nano Lett.*, **18**, 853 (2018)], tailored emission from two-dimensional semiconductor materials [*Nano Lett.* **15**, 3578 (2015), *ACS Phot.* **5**, 552 (2018)] and strong coupling.

8:40am **EM+MI+MN+NS-ThM3 The Geode Process: A Route to the Large-Scale Manufacturing of Functionally-Encoded Semiconductor Nanostructures**, M. Mujica, G. Tutuncuoğlu, V. Breedveld, S.H. Behrens, **Michael Filler**, Georgia Institute of Technology

Future large-area electronic and photonic technologies will require the manufacturing of materials and devices at very high rates without sacrificing nanoscale control of structure and composition. Semiconductor nanowires, for example, can be produced with exquisite spatial control of composition and morphology using the vapor-liquid-solid (VLS) mechanism that, however, remains limited to very small manufacturing rates. Here, we introduce the Geode process to synthesize functionally-encoded semiconductor nanowires at throughputs orders of magnitude beyond the state-of-the-art. Central to the Geode process are sacrificial, porous-walled, seed particle-lined silica microcapsules, whose interior surface serves as a high-surface area growth substrate. Microcapsules protect the growing nanostructures, are produced with a scalable emulsion templating technique, and are compatible with large-scale chemical reactors. We will show how microcapsule structure and drying is influenced by silica nanoparticle type and concentration, emulsification parameters, and nanoparticle cross-linking agent. We will also demonstrate the synthesis of Si nanowires with programmable dopant profiles on the microcapsule interior, which not only shows the versatility of the process, but also allows the impact of precursor gas transport limitations to be characterized.

9:00am **EM+MI+MN+NS-ThM4 Disordered Microsphere-Based Coatings for Effective Radiative Cooling under Direct Sunlight**, S. Atiganyanun, J. Plumley, K. Hsu, University of New Mexico; T.L. Peng, Air Force Research Laboratory; **Sang M. Han**, S.E. Han, University of New Mexico

Radiative cooling is a process where a material loses heat due to strong emission of photons in the mid-infrared spectrum and enhanced light scattering in the solar region. This process would allow cooling of materials below the ambient temperature under the sun without the use of electricity and therefore would significantly reduce energy consumption. In this work, we have demonstrated a passive radiative cooling of disordered silica microsphere coatings below the ambient temperature while exposed to direct sunlight. To fabricate the coatings, silica microspheres are deposited by colloidal sedimentation method and spray coating method. In the first method, silica colloidal stability is disrupted by addition of KCl solution. The instability causes the colloids to agglomerate and sediment, creating a disordered uniform coating. In the second method, much like commercial painting, the colloidal solution is forced through a spray nozzle and deposited onto a substrate. Scanning electron microscopy show that the resulting structures are disordered without short- or long-range order. Optical measurements also indicate that the coatings produced under optimal conditions have a short transport photon mean free path of approximately 4-8 μm in the solar spectral region. These coatings also exhibit high emissivity above 95% in the atmospheric transparency window. These results suggest strong photon scattering properties in the visible region, while providing a strong thermal emission. Such films would enable effective radiative cooling. To test the cooling performance, we apply this film on top of a black substrate and expose the material to a direct sunlight during the summer in New Mexico. Temperature measurement of the samples shows that our coating reduces the substrate temperature below that of the ambient air by as much as 12 °C during daytime. Similar testing with a commercial solar-rejection paint indicates that the silica coating performs better than the commercial paint by 4.7 °C on average. Additionally the similar technique is used to fabricate disordered coatings made of polystyrene-polymethyl methacrylate microspheres. Outdoor experiments have shown that the polymer coatings

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perform better than the commercial paint by 5.5 °C on average. Disordered coatings made of microspheres in a paint format will also be discussed.

9:20am **EM+MI+MN+NS-ThM5 Assessing Strain Relaxation in Nanostructured InGaN Multiple Quantum Wells Using X-Ray Diffraction Reciprocal Space Mapping and Photoluminescence Spectroscopy, Ryan Ley, C.D. Pynn, M. Wong, S.P. DenBaars, M.J. Gordon, University of California at Santa Barbara**

The III-Nitrides are excellent materials for LEDs, lasers and power electronics due to their tunable bandgap and high defect tolerance. These materials are increasingly important for displays in mobile and portable electronic devices, which currently suffer from short battery lives because displays based on liquid crystals or organic LEDs are inefficient. Producing high quality III-Nitride material with the indium compositions needed for efficient green and red emission is presently very challenging, due in large part to strain effects resulting from the large lattice mismatch between InGaN and GaN. However, there are some indications that nanostructuring can reduce or eliminate some of these strain issues.

This talk will highlight our recent work using colloidal and templated lithography and Cl<sub>2</sub>/N<sub>2</sub> plasma etching to fabricate nanoscale InGaN/GaN LED structures (diameter = 150-600nm), and how sub micron scale patterning affects the strain state and optical behavior of MQW emitters. InGaN/GaN LED structures were grown by MOCVD on c-plane sapphire substrates and characterized before and after nanopatterning using on-axis (0002) and off-axis (10-15 and 11-24) XRD reciprocal space maps (RSM), rocking curves and photoluminescence (PL) spectroscopy at 14K. RSM analysis found degrees of relaxation of 30% and 20% for the smallest and largest structures, respectively, and rocking curves revealed a 0.7nm decrease in the InGaN quantum well thickness. These relaxation effects also correlate well with spectral blue shifts (~10-15nm) in the PL, which are supported by 1D quantum mechanical and electrostatic simulations. Overall, this work shows that nanopatterning of InGaN/GaN active emitters at sub-micron length scales can reduce strain related issues in the III-Nitrides and potentially allow higher incorporation of indium for green and red emission.

9:40am **EM+MI+MN+NS-ThM6 Scalable, Tunable, and Polarization-Independent High Contrast Grating Reflectors for Integration into Resonant-Cavity micro-LEDs, Pavel Shapturenka, S.P. DenBaars, M.J. Gordon, University of California at Santa Barbara**

III-nitride blue and green micro-LEDs have exhibited quantum efficiencies of over 40%, which is a nearly fivefold efficiency boost over current OLED and LCD digital display technologies. In order to realistically continue LED miniaturization below 10 microns for high-resolution and near-eye pixel displays, it is necessary to maintain emission directionality and output power. One method to accomplish this is to make a resonant-cavity micro-LED device with a high-reflectance mirror and an output coupler.

We demonstrate a low-cost, tunable, and scalable colloidal lithography method to fabricate suspended TiO<sub>2</sub> high-contrast grating (HCG) reflectors across the visible wavelength range for eventual integration as an output coupler in a resonant-cavity LED. Silica spheres (310-960 nm diameter), deposited via Langmuir-Blodgett dip-coating, were used as a mask to define a quasi-ordered, hexagonal pattern on a 200 nm thick TiO<sub>2</sub> film.

Subsequent pattern transfer with SF<sub>6</sub> reactive ion and XeF<sub>2</sub> chemical etching of sacrificial Si layers beneath the TiO<sub>2</sub> layer yielded a periodic, high index contrast between the suspended array structure and the surrounding air medium. Near-normal-incidence reflectance measurements on structures of increasing hole pitch (310-960 nm) showed an increase in maximum reflected wavelength from 370 to >1000 nm, while maintaining a high-%R bandwidth of 40-100 nm. The reflectance was also observed to be polarization-independent. Finite-difference time domain (FDTD) simulations of structural imperfection stemming from the colloidal lithography process, e.g., deviations in hole diameter, pitch, and hexagonal symmetry, indicate that absolute reflectance is most affected by hole offset from hexagonal lattice positions. The talk will highlight processing methods, optical characterization of HCGs, and underlying trends in the effect of HCG geometry on optical response as predicted by FDTD simulations. This work suggests that scalable fabrication of visible-wavelength HCGs is feasible and holds promise for integration into resonant-cavity LEDs.

11:00am **EM+MI+MN+NS-ThM10 Nano-optical Activation of Defect-bound Excitons in Monolayer WSe<sub>2</sub>: Towards Room-temperature 2D Single-photon Optoelectronics, Jim Schuck, Columbia University INVITED**

The emergence of two-dimensional (2D) monolayer transition metal dichalcogenides (1L-TMDC) as direct bandgap semiconductors has rapidly accelerated the advancement of room temperature, 2D optoelectronic devices. Optical excitations on the TMDCs manifest from a hierarchy of electrically tunable, Coulombic free-carrier and excitonic many-body phenomena. In our most recent nano-optical investigations of these materials, we have demonstrated that a model hybrid architecture, a nano-optical antenna and a 1L-WSe<sub>2</sub> nanobubble, activates the optical activity of BX states at room temperature and under ambient conditions. These results show that engineered bound-exciton functionality as, in this case, localized nanoscale light sources, can be enabled by an architectural motif that combines localized strain and a nano-optical antenna, laying out a possible path for realizing room-temperature single-photon sources in high-quality 2D semiconductors.

11:40am **EM+MI+MN+NS-ThM12 Light Scattering Properties of Silver Nanoprisms in Different Environments, Yuri Strzhemechny, Texas Christian University; S. Requena, Harris Night Vision; H. Doan, Texas Christian University; S. Raut, University of North Texas Health Science Center; Z. Gryczynski, Texas Christian University; I. Gryczynski, University of North Texas Health Science Center**

Embedding nanostructures into different environments, such as polymer matrices, organic and biological solutions oftentimes produces unique optoelectronic properties of the resulting compound system that are distinct from those of the host and nano-filler. Such strong modifications can be caused by the interface phenomena, the change in the spatial distribution and orientation of the nanostructures or a combination thereof. In this work, we report on optical properties of silver triangular prism nanoparticles embedded in water, lipid solutions, and polyvinyl alcohol (PVA) polymer thin films. For our studies, using a common chemical reduction routine, we synthesized, batches of silver nanoparticles with different size distributions and distinct size-dependent dipole resonance spectra. Silver nanoprisms suspended in water yielded a noticeable wavelength-dependent depolarization of scattered light associated with different surface plasmon modes. Consequently, the same nanostructures were placed into lipid environments to estimate the rejection of a polarized background scattering during depolarization measurements. After that, the composite thin films were fabricated via incorporation of silver nanoparticles into PVA. We studied linear dichroism in those Ag/PVA films, as-prepared and subjected to controllable stretching. Re-orientation of the nanoprisms upon stretching leads to a significant increase of the linear dichroism for the plasmonic modes associated with the in-plane dipole oscillations and a decrease of the linear dichroism corresponding to the out-of-plane plasmonic modes. These observations are in good agreement with the assumption that stretching of the nanocomposite films leads to an anisotropic realignment of the nanoprisms.

12:00pm **EM+MI+MN+NS-ThM13 Core-Shell Processing of BTO Nanocomposites for Optimal Dielectric Properties, Kimberly Cook-Chennault, Rutgers University**

High permittivity polymer-ceramic nanocomposite dielectric films leverage the ease of flexibility and processing of polymers and functional properties of ceramic fillers. Physical characteristics of these materials can be tuned for application to a variety of applications, such as, advanced embedded energy storage devices for printed wired electrical boards and battery separators. In some cases, the incompatibility of the two constituent materials; hydrophilic ceramic filler and hydrophobic epoxy can limit the filler concentration and therefore, dielectric properties of these materials. Use of surfactants and core-shell processing of composite fillers is traditionally used to achieve electrostatic and steric stabilization for adequate ceramic particle distribution. This work aims to understand the role of surfactant concentration in establishing meaningful interfacial layers between the epoxy and ceramic filler particles by observing particle surface morphology, dielectric permittivity and device dissipation factors. A comprehensive study of nanocomposites that were comprised of non-treated and surface treated barium titanate (BT) embedded within an epoxy matrix was performed. The surface treatments were performed with ethanol and 3-glycidyloxypropyltrimethoxysilan, where the best distribution, highest value of permittivity (~ 48.03) and the lowest value of loss (~0.136) were observed for the samples that were fabricated using 0.5 volume fraction of BaTiO<sub>3</sub> and 0.02 volume fraction of silane coupling agent.

## MEMS and NEMS Group

Room 202B - Session MN+2D+AN+MP+NS-ThM

### Optomechanics and 2D NEMS

**Moderator:** Max Zenghui Wang, University of Electronic Science and Technology of China

8:00am **MN+2D+AN+MP+NS-ThM1 Towards Microwave to Telecom Wavelength Quantum Information Transfer using Cavity Optomechanics, John Davis**, University of Alberta, Canada **INVITED**

The past few years have seen the rapid maturation of quantum information processors, particularly in the category of superconducting microwave circuits. With claims from leading companies that they will commercialize quantum processors in the next five years, we must wonder what quantum technologies should be developed in tandem to fully utilize these processors. For example, we are all acutely aware that while our personal computers are powerful, they are considerably more useful and interesting when networked together. So how can we likewise network quantum processors? Especially since the microwave signals of superconducting processors cannot be transmitted at room temperature without thermal decoherence. What if instead, one could link superconducting processors together through existing fiber-optic networks, which are already capable of long distance quantum information transfer? Hence the development of a transducer of quantum information from the microwave to telecom domain has become highly desirable. I will describe the current state of microwave to optical transducers, and how our lab is working towards this goal. Specifically, I will discuss the progress and challenges associated with the development of fiber-coupled telecom-wavelength cavity optomechanical resonators, and 3D superconducting microwave cavities, operating at millikelvin temperatures. I will also discuss ongoing collaborations that could enable implementation of quantum information transducers in a large-scale fiber network in Alberta.

11:20am **MN+2D+AN+MP+NS-ThM11 Reconfigurable Resonant Responses in Atomic Layer 2D Nanoelectromechanical Systems (NEMS), Zenghui Wang**, University of Electronic Science and Technology of China; *R. Yang, P.X.-L. Feng*, Case Western Reserve University

Atomic layer semiconducting crystals have emerged as a new class of two-dimensional (2D) materials, exhibiting great promises for both fundamental research and technological applications. Their outstanding electromechanical properties make these materials ideal for constructing novel 2D NEMS, providing opportunities for leveraging their unique device properties across multiple information-transduction domains, at scales down to individual atomic layers. One particularly interesting category of 2D NEMS is 2D nanoelectromechanical resonators, which hold potentials for making the next generation RF signal transduction and processing components, with miniaturized size, ultra-low power consumption, and compatibility with transparent and flexible circuits.

Towards future applications in the 5G era, multi-band RF signal handling capability is desired, as the number of bands each mobile device need to have access to significantly increases, and it would be impractical to simply increase the number of RF components that can only function under one RF frequency, as the space required for mounting such components scales with the number of bands. Therefore, ultralow-power tunable and reconfigurable RF devices that can adapt to different frequencies would be one solution to this challenge.

Here we present experimental demonstration of nanomechanical resonators based on layered MoS<sub>2</sub> atomic crystals that have reconfigurable resonant responses. By carefully studying the temperature-dependent frequency response in such MoS<sub>2</sub> resonators[1], we discover clear, repeatable hysteretic behavior as the device temperature is changed[2]. Leveraging this phenomenon, we achieve switchable resonance frequency  $f_{res}$  in such devices by using heating and cooling pulses. Specifically, for an example MoS<sub>2</sub> resonator, during heating pulses, the  $f_{res}$  decreases to ~20MHz. Once the device recovers to room temperature,  $f_{res}$  stabilizes at ~26MHz. During cooling pulses,  $f_{res}$  increases to ~29MHz, and upon reverting to room temperature  $f_{res}$  stays at ~24.5MHz, which is clearly different than the other room temperature state. Our findings suggest that such atomic-layer MoS<sub>2</sub> NEMS resonators could be used towards developing reconfigurable RF components whose frequency response can be switched between different states.

[1] R. Yang, et al., *IEEE UFFC*, pp 198-201, 2015. [2] Z. Wang, et al., *IEEE UFFC*, pp 783-786, 2015.

11:40am **MN+2D+AN+MP+NS-ThM12 Cavity Optomechanics: Dynamics and Applications, Eyal Buks**, Israel Institute of Technology, Israel **INVITED**  
The field of cavity optomechanics deals with a family of systems, each composed of two coupled elements. The first one is a mechanical resonator, commonly having a low damping rate, and the second one is an electromagnetic cavity, which typically is externally driven. Both radiation pressure and bolometric force can give rise to the coupling between the mechanical resonator and the cavity. In recent years a variety of cavity optomechanical systems have been constructed and studied, and phenomena such as mode cooling, self-excited oscillation, and optically induced transparency have been investigated. The first part of the talk will be devoted to some dynamical effects including synchronization and intermittency. In the second part some applications of optomechanical cavities for sensitive sensing will be discussed.

## Nanometer-scale Science and Technology Division

Room 102B - Session NS+AN+EM+MI+MN+MP+PS+RM-ThM

### Nanopatterning and Nanofabrication

**Moderators:** Brian Hoskins, National Institute of Standards and Technology (NIST), Meredith Metzler, University of Pennsylvania, Leonidas Ocola, IBM Research Division, T.J. Watson Research Center

8:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM1 Femtosecond Laser Processing of Ceria-Based Micro Actuators, J. Shklovsky**, Tel Aviv University, Israel; *E. Mishuk*, Weizmann Institute of Science, Israel; *Y. Berg*, Orbotech Ltd, Israel; *N. Vengerovsky, Y. Sverdlov*, Tel Aviv University, Israel; *I. Lubomirsky*, Weizmann Institute of Science, Israel; *Z. Kotler*, Orbotech Ltd; *S. Krylov, Y. Shacham-Diamand, Erez Benjamin*, Tel Aviv University, Israel

The integration of piezoelectric and electrostrictive materials into micromachined Si devices is viewed as an important technological milestone for further development of Microelectromechanical Systems (MEMS). Recently, it was demonstrated that gadolinium-doped ceria (CGO) exhibits very large electrostriction effect, which results in large electrostrictive strains and high energy densities under very low frequencies (0.01 – 1 Hz). Lead-free CGO is chemically inert with respect to Si, making it an attractive candidate for implementation in MEMS actuators. However, the integration of CGO into MEMS devices is challenging due problems associated with using conventional patterning techniques involving lithography and etching.

In this work, we have successfully created functional double-clamped beam micro-actuators made of CGO films confined between the top and bottom Al/Ti electrodes. The stack containing the electrodes and the  $\approx 2 \mu\text{m}$ -thick CGO film was first blanket-deposited on top of the Si wafer. Cavities were then deep reactive ion etched (DRIE) in the wafer leading to forming of the free-standing rectangular membranes, 1.5 mm  $\times$  0.5 mm in size. Finally,  $\approx 1.2 \text{ mm}$  long and  $\approx 100 \mu\text{m}$  wide the double-clamped beams were cut from the membranes using a femtosecond (fs) laser, demonstrating an unharmed technique for CGO patterning. Laser pulse energies, overlaps and number of line passes were varied during the experiments, to achieve successful cuts through the suspended layer by a clean ablation process. The optimized process conditions were found at a fluence of  $\sim 0.3 \text{ J/cm}^2$  for a pulse width of 270 fs, where minimal damage and accurate processing was achieved with minimized heat-affected zones.

Resistivity measurements between the top and the bottom electrodes before and after fs laser cutting revealed that the cutting has no influence on the electric parameters of the device and no electrical shorts are introduced by the laser processing. Vertical displacement measurements under bipolar AC voltage (up to 10 V), at the frequency range of 0.03 – 2 Hz, demonstrated the functionality of the micro-actuator. A displacement of  $\approx 45 \text{ nm}$  at the voltage of 10 V at 50 mHz was achieved. The actuator didn't show any mechanical or electrical degradation after continuous operation. Our data confirm that fs laser cutting is a useful technique for processing CGO films. The developed techniques may be expanded to other materials used for fabrication of MEMS devices, enabling fast, high yield and high-quality patterning of materials that are challenging to pattern using conventional etching-based methods.

\*Three first authors contributed equally to this abstract.

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8:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM2 Synthesis of Functional Particles by Condensation and Polymerization of Monomer Droplets in Silicone Oils**, *Prathamesh Karandikar, M. Gupta*, University of Southern California

The initiated chemical vapor deposition (iCVD) process is an all-dry, vacuum process used to deposit a wide variety of functional polymers. Typically, the monomer and initiator radicals are introduced simultaneously at process conditions leading to undersaturation of monomer vapors. In this work we report a sequential vapor phase polymerization method in which monomer droplets were first condensed onto a layer of silicone oil and subsequently polymerized via a free radical mechanism to fabricate polymer particles.

The viscosity of the silicone oil was systematically varied from 100 cSt through 100,000 cSt. A heterogeneous particle size distribution was produced at low viscosities of silicone oil where the smaller particles were formed by the cloaking and engulfment of monomer droplets nucleated at the vapor-liquid interface and the larger particles were formed by coalescence inside the liquid. Coalescence could be inhibited by increasing the viscosity of the silicone oil leading to a decreased average radius and a narrower size distribution of the polymer particles. A transition to polymer film formation was observed for the 100,000 cSt silicone oil substrates. We studied the polymerization of two different monomers, 4-vinyl pyridine and 2-hydroxyethyl methacrylate, since these polymers have a variety of useful properties such as pH-responsiveness and biocompatibility. Our process enables fabrication of functional particles with average diameters ranging from 100 nm – 500 nm with fast reaction times ( $\approx 15$  min). The advantages of our method for the fabrication of polymer particles are that it does not require surfactants or organic solvents and features short reaction times compared to conventional polymer particle synthesis methods such as emulsion polymerization.

8:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM3 Competition Between Scale and Perfection in Self-assembling Structures**, *James Liddle*, NIST Center for Nanoscale Science and Technology **INVITED**

Biology relies on self-assembly to form complex, highly-functional structures, inspiring the search for synthetic systems capable of forming similarly complex structures. Such systems typically operate under diffusion-limited, near-equilibrium conditions, making the problem even more challenging. Multi-functional, molecularly-addressable nanostructures of arbitrary shape can be built using DNA-mediated self-assembly. While this is a powerful method, and recent developments in DNA nanostructure fabrication have expanded the available design space, fabrication based on DNA alone can suffer from low yields and is hampered by the need to trade off size and mechanical rigidity.[1,2]

We have been working to both understand the factors that limit the yield of self-assembled structures, and to devise approaches to overcome them. As the number of discrete components used to assemble a structure increases, yield decreases exponentially. We circumvent this limit, by using a two-stage, hierarchical self-assembly process, which allows us to create large structures with high yield.[3] Our process employs a small number of discrete, sequence-specific elements to shape the structure at the nanoscale and define the large-scale geometry. A generic building block – a DNA binding protein, *RecA* – rigidifies the structure without requiring any unnecessary information to be added to the system.

Blending sequence-specific and structure-specific elements enables us to expand the self-assembly toolbox and make micrometer-scale, rigid, molecularly-addressable structures. More generally, our results indicate that the scale of finite-size self-assembling systems can be increased by minimizing the number of unique components and instead relying on generic components to construct a framework that supports the functional units.

[1] Murugan, A., Zou, J. & Brenner, M. P. Undesired usage and the robust self-assembly of heterogeneous structures. *Nat. Commun.* **6**, 6203, doi:10.1038/ncomms7203 (2015).

[2] Schiffels, D., Liedl, T. & Fygenon, D. K. Nanoscale structure and microscale stiffness of DNA nanotubes. *ACS Nano* **7**, 6700-6710, doi:10.1021/nn401362p (2013).

[3] Schiffels, D., Szalai, V. A., Liddle, J. A., Molecular Precision at Micrometer Length Scales: Hierarchical Assembly of DNA-Protein Nanostructures, *ACS Nano*, **11**, 6623, (2017)

9:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM5 Polymer Templated Annealing of DNA Patterned Gold Nanowires**, *Tyler Westover, B. Aryal, R.C. Davis, A. Woolley, J. Harb*, Brigham Young University

Using DNA origami as a bottom up nanofabrication technique, gold nanowires are formed via directed assembly of gold nanorod seeds and connected by electroless plating. This metal deposition process results in wires with low conductivities compared to bulk gold. Junctions between plated seeds are likely the cause of this low conductivity. Annealing of the nanowires could potentially improve the conductance, however, nanowire annealing at low temperatures (200° C) results in wires coalescing into beads. A polymer encapsulation layer was deposited to maintain overall nanowire shape during annealing. The polymer templated anneal resulted in a resistance reduction, in some cases, to below 1000 ohms. Resistance measurements were performed using a four point resistance configuration. Electrical contacts to the randomly oriented 400 nm long wires were made by electron beam induced deposition. Nanowire morphology was measured before and after annealing by scanning electron and high resolution transmission electron microscopy.

11:00am **NS+AN+EM+MI+MN+MP+PS+RM-ThM10 Directed Self-assembly of Block Copolymers for Applications in Nanolithography**, *Paul Nealey*, University of Chicago **INVITED**

DSA of block copolymer films on chemically nanopatterned surfaces is an emerging technology that is well-positioned for commercialization in nanolithography and nanomanufacturing. DSA of (PS-*b*-PMMA) films on lithographically defined chemically nanopatterned surfaces is one focus of our activities in which the main research objectives revolve around understanding the fundamental thermodynamics and kinetics that governs assembly, and therefore patterning properties such as 3D structure, perfection, and processing latitude. A second focus is to use the physical and chemical principles that we have elucidated for DSA of PS-*b*-PMMA towards the development of block copolymer systems capable of self-assembling into the sub 10 nm regime and continuing to meet the stringent constraints of manufacturing. The research is enabled by the recent development of techniques to combine metrology tools (TEM tomography, GISAXS, RSoXS, high-speed APF), theoretically informed coarse grained models, and evolutionary algorithms to quantitatively determine and predict the independent process and material parameters that result in different 3D structures of assembled domains.

11:40am **NS+AN+EM+MI+MN+MP+PS+RM-ThM12 Three Dimensional Mesoporous Silica Nanowire Network Fabricated by Metal-Assisted Chemical Etching**, *Deepak Ganta, C. Guzman, R. Villanueva*, TAMIU

Mesoporous nanowires have gained huge attention due to their applications in energy and sensing. The high surface area along with the quantum confinement effect lead to improved performance of the electrochemical devices during energy conversion and storage. 3D structure or nanowire network improves the reaction site surface area even further along all the three dimensions, enhancing both light and heat absorption. There is also a huge demand for inexpensive, non-lithographic methods to fabricate 3D network of nanowires, which are also mesoporous, with better control of both dimensions and porosity, over a large surface area. They can be very useful in some broad range applications such as solar energy conversion, energy storage, water harvesting, environmental control, bio-sensing, and thermoelectrics.

To address the problem, we report a simple and inexpensive method of fabricating 3D mesoporous Si nanowire network by metal-assisted chemical etching (MacEtch). Degenerately doped p-type silicon or p+ silicon wafer (0.001 ~0.005  $\Omega$ -cm) was coated with about 22 nm silver film at 350 °C for 5~6 hours in a vacuum furnace (pressure < 3 $\times$ 10<sup>-7</sup> Torr). Scattered silver particles with different sizes were formed as a result of the dewetting process. Then we deposited 10~11 nm of noble metal (Au) at 0.5 Å/s rate, followed by silver lift-off to obtain an Au mesh as an etching mask. The mixture of a chemical solution of HF: H<sub>2</sub>O<sub>2</sub>: Ethanol = 30:1:1 is used as a chemical etchant under room temperature. The time of immersion of the silicon wafer in the etchant effects the aspect ratio of the silicon nanowire array. After MachEtch, the Au is removed by immersing the sample in the aqua regia solution. The ratio of the chemicals in the etchant will affect the

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pore size. The aspect ratio of the silicon nanowire network can be controlled by the etching rate. The etching rate was roughly one  $\mu\text{m}/\text{min}$ . The 3D network is formed as the length of the 1D silicon nanowires (50 nm -100 nm) was varied, followed by critical point drying to carefully control the uniformity of 3D silicon nanowire network on the entire surface area of the 6-inch silicon wafer.

Analysis of the 3D mesoporous silicon nanowire network was conducted using Scanning Electron microscopy (SEM), and the top view image confirmed the 3D network of silicon nanowires. The pore sizing (2-50 nm) along with the crystallinity confirmed from the high-resolution transmission electron microscopy (TEM) images with the diffraction patterns.

12:00pm **NS+AN+EM+MI+MN+MP+PS+RM-ThM13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring**, *L. Chan, C.D. Pynn, S.P. DenBaars, Michael Gordon*, University of California at Santa Barbara

A simple, scalable, and reproducible nanopatterning method to create close-packed (moth-eye like) patterns of conical nano- and microscale features on InGaN/GaN LED surfaces, and on the backside outcoupling surface of LED devices, is presented. Colloidal lithography via Langmuir-Blodgett dip-coating using silica masks ( $d = 170\text{--}2530\text{ nm}$ ) and  $\text{Cl}_2/\text{N}_2$ -based plasma etching produced features with aspect ratios of 3:1 on devices grown on semipolar (20-21) GaN substrates. The resulting InGaN/GaN multi-quantum well (MQW) structures were optically pumped at 266/405 nm, and light extraction enhancement was quantified using angle-resolved photoluminescence (PL). A 4.8-fold overall enhancement in light extraction (9-fold at normal incidence) relative to a flat outcoupling surface was achieved using a feature pitch of 2530 nm. Extraction enhancement occurs due to the graded-index (GRIN) effect and breaking of the TIR condition via increased diffuse scattering and diffractive effects, the importance of which evolves with moth-eye feature size. PL results also demonstrate that colloidal roughening, which has greater geometric tunability and works on any GaN orientation, is equivalent to current, c-plane only photoelectrochemical (PEC) roughening methods. Patterning the outcoupling backside of a semipolar device, rather than the topside, is also a technologically feasible approach to fabricate electrically pumped devices because it avoids issues associated with making large area (topside) p-contacts, etching close to or into the active emitter region (destroying the MQWs), or disrupting guided modes in thin-film LEDs layers on sapphire. Because of its simplicity, range of optical control, and wide substrate compatibility, the colloidal lithography technique is a promising alternative to existing commercial processes and a future pathway for enhanced extraction engineering in free-standing polar, nonpolar, and semipolar III-nitride LEDs.

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## 2D Materials Focus Topic

### Room 201B - Session 2D+EM+MN+NS-ThA

#### Novel Quantum Phenomena in 2D Materials

**Moderator:** Hsin Lin, Institute of Physics, Academia Sinica

2:20pm **2D+EM+MN+NS-ThA1 Double Indirect Interlayer Exciton in a MoSe<sub>2</sub>/WSe<sub>2</sub> van der Waals Heterostructure**, *Aubrey Hanbicki, H.-J. Chuang, M. Rosenberger, C.S. Hellberg, S.V. Sivaram, K.M. McCreary, I. Mazin, B.T. Jonker*, Naval Research Laboratory

Tailoring semiconductor heterostructures for specific functionalities has led to varied opto-electronic devices including solar cells, photodetectors, light-emitting diodes and lasers. An emerging class of heterostructures involves monolayer semiconductors such as many of the transition metal dichalcogenides (TMDs) which can be combined to form van der Waals heterostructures (vdWHs). vdWHs offer novel functionalities making them promising hosts for future devices. One unique new heterostructure property is an interlayer exciton (ILE), a spatially indirect, bound electron-hole pair with the electron in one TMD layer and the hole in the other. Here, using state-of-the-art preparation techniques, we are able to resolve emission from the ILE in a MoSe<sub>2</sub>/WSe<sub>2</sub> heterostructure into two distinct peaks separated by 24 meV at zero field. These peaks have nearly equal intensity, indicating they are of common character, and have *opposite* circular polarizations when excited with circularly polarized light. *Ab initio* calculations successfully account for these observations – they show that both emission features originate from excitonic transitions that are indirect in momentum space and are split by spin-orbit coupling. Also, the electron is strongly hybridized between both the MoSe<sub>2</sub> and WSe<sub>2</sub> layers, with significant weight in both layers, contrary to the commonly assumed model. Thus, the transitions are not purely interlayer in character. This work represents a significant advance in our understanding of the static and dynamic properties of TMD heterostructures.

This research was performed while H.-J.C. held an American Society for Engineering Education fellowship and M.R.R and S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL and the NRL Nanoscience Institute. This work was also supported in part by a grant of computer time from the DoD High Performance Computing Modernization Program at the U.S. Army Research Laboratory Supercomputing Resource Center.

2:40pm **2D+EM+MN+NS-ThA2 Comparison of A- and B-exciton Intensity and Polarization in Transition Metal Dichalcogenide Monolayers and Heterostructures**, *Kathleen McCreary, A.T. Hanbicki, S.V. Sivaram, B.T. Jonker*, U.S. Naval Research Laboratory

We survey a large number of monolayer TMDs to better understand the conditions responsible for various emission characteristics that have been reported in literature. We find that the intensities for both A- and B- peak emission vary widely as a result of sample-to-sample variations. However, a measurable B-peak intensity is evident in all samples. There is a clear linear relationship between the two peak intensities. The emission from the dominant A-peak is commonly several orders of magnitude higher than B-peak emission, resulting in B/A-intensity ratios well below 1%. Yet, as the A-peak intensity decreases, the ratio of B/A monotonically increases, and we observe a B/A ratio up to 30% in monolayer MoS<sub>2</sub>. The A-excitonic emission is further quenched when MoS<sub>2</sub> is incorporated into an MoS<sub>2</sub>/MoSe<sub>2</sub> heterostructure, where we observe comparable A- and B-peak intensities. We attribute these variations to differences in exciton recombination times, clarifying contradictory reports regarding the accessibility and significance of B-peak emission. Furthermore, we observe a high degree of valley polarization in both B-exciton emission in isolated monolayers and A-exciton emission in heterostructures, consistent with our model detailing the rapid exciton lifetimes in B-emission and van der Waals heterostructures.

Supported by core programs at NRL and the NRL Nanoscience Institute

3:00pm **2D+EM+MN+NS-ThA3 Optospintronics and Magnetism with 2D Materials and Heterostructures**, *Roland Kawakami*, The Ohio State University

**INVITED**

I will review our latest developments in spintronics, optospintronics and magnetism in two-dimensional (2D) materials and heterostructures. Graphene continues to exhibit improved properties for spin transport and demonstrates additional functionality through the use of vertically stacked heterostructures. One of the interesting new directions is optospintronics enabled by heterostructures of graphene and transition metal dichalcogenides (TMD) [1]. Due to the valley optical selection rules of TMDs

and the large spin-orbit coupling, the helicity of the photon is coupled to the valley spin polarization of electrons. Thus, circularly polarized optical excitation into a TMD/graphene heterostructure generates spin polarization in the TMD that subsequently transfers to the graphene. This optical spin injection into graphene is an example of new functionality for the expanding field of 2D spintronics. In the area of 2D magnets, we have used molecular beam epitaxy (MBE) to deposit monolayer MnSe<sub>2</sub>, which exhibits ferromagnetism at room temperature [2]. These results open the door for new possibilities for magnetoelectronic applications with low dimensional materials.

[1] Yunqiu Kelly Luo, Jinsong Xu, Tiancong Zhu, Guanzhong Wu, Elizabeth J. McCormick, Wenbo Zhan, Mahesh R. Neupane, and Roland K. Kawakami, *Nano Lett.* 17, 3877 (2017).

[2] Dante J. O'Hara, Tiancong Zhu, Amanda H. Trout, Adam S. Ahmed, Yunqiu Kelly Luo, Choong Hee Lee, Mark R. Brenner, Siddharth Rajan, Jay A. Gupta, David W. McComb, and Roland K. Kawakami, *Nano Lett.* doi: 10.1021/acs.nanolett.8b00683 (2018).

4:00pm **2D+EM+MN+NS-ThA6 Giant Electromechanical Response in Van-der-Waals Layered Crystals**, *Sabine Neumayer*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory; *E.A. Eliseev*, National Academy of Sciences of Ukraine; *A. Tselev*, CICECO and Department of Physics, University of Aveiro, Portugal; *A.N. Morozovska*, National Academy of Sciences of Ukraine; *M.A. Susner, M.A. McGuire*, Oak Ridge National Laboratory; *J. Brehm, S. Pantelides*, Vanderbilt University; *N. Balke, P. Maksymovych*, Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Obtaining ultrathin electromechanically active materials for memory and energy applications encounters numerous challenges as significant downscaling of classical ferroelectrics such as perovskite oxides is severely constrained by size and screening effects. Moreover, interfacing pseudocubic ferroelectrics with 2D electronic materials faces challenges related to defect and impurities, which limit performance. Van der Waals ferroelectrics, especially transition metal thiophosphates such as copper indium thiophosphate (CIPS) yield promising prospects for applications as ultrathin piezoelectric structures and interface materials due to their stable surfaces, layered structure and transition temperatures near room temperature. Here, we use scanning probe microscopy to explore the remarkable functional properties of CIPS across the transition temperature. At low temperatures, strong electromechanical response is measured despite the small polarization values and the material contracts in electric fields rather than expanding. These findings point to giant negative electrostrictive coefficients, which were quantified using Landau-Ginzburg-Devonshire analysis. Above the transition temperature, CIPS shows dielectric tunability comparable to BST at low frequencies. In addition, electromechanical strain exceeding 10 nm displacement was measured upon fully reversible field induced formation of particles on the surface. Complimentary DFT calculations provide further insight into the role of ionic displacement in electromechanical behavior.

Research conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility. Research was sponsored by the Laboratory Directed Research and Development Program of Oak Ridge National Laboratory, managed by UT-Battelle, LLC, for the U. S. Department of Energy.

4:20pm **2D+EM+MN+NS-ThA7 A Universal Method for Measuring Valleytronic Quality of 2D Materials using Conventional Raman Spectroscopy**, *Steven Vitale, J.O. Varghese, D.A. Nezich, M. Rothschild*, MIT Lincoln Laboratory

Valleytronics offers a new information processing paradigm based on the momentum index of real or quasi-particles in 2D materials as the fundamental unit of information storage instead of charge. A major challenge to realize valleytronic computing is the development of deterministic material growth processes which yield valleytronic-quality material with the requisite valley relaxation lifetime (T<sub>1</sub>) and valley dephasing time (T<sub>2</sub>). Unfortunately direct measurement of T<sub>1</sub> and T<sub>2</sub> requires complex instrumentation to perform ultrafast spectroscopic measurements and thus is not practical for routine material analysis. In this paper, we demonstrate that an accurate and reproducible measurement of T<sub>1</sub>/T<sub>exc</sub> (where T<sub>exc</sub> is the exciton recombination lifetime) can be performed a simple Raman microscope. By simultaneously measuring the photoluminescence of the 2D material and the Raman transition of the underlying silicon substrate as a function of the incident laser polarization angle, one can remove sources of error and equipment-to-equipment variability. This technique is completely general and can be applied to any

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valleytronic material which can be grown-on or transferred-to a Raman-active crystalline substrate, such as silicon. Using this technique we show that valley relaxation in a sample of CVD-grown MoS<sub>2</sub> is an order of magnitude slower at 4 K than at 100 K. Oxidation of MoS<sub>2</sub> left exposed to the ambient environment severely decreases the valleytronic quality of the material. Two-dimensional mapping of the valley relaxation time of CVD

MoS<sub>2</sub> domains at 4 K shows a three-fold spatial symmetry which is suggestive of new valley physics phenomena which arise in 2D crystals of finite size. MoS<sub>2</sub> domain size also affects the valley relaxation time, which has significant material-growth implications for real valleytronic applications. Finally we compare these measurements to our calculated requirements for valley relaxation time in a practical information processing device and quantify the challenges for future valleytronic material growth.

4:40pm **2D+EM+MN+NS-ThA8 Discovery of Intrinsic Ferromagnetism in 2D van der Waals Crystals**, *Xiang Zhang, C. Gong*, University of California, Berkeley **INVITED**

In this talk, I will present our discovery of the intrinsic ferromagnetism in 2D van der Waals (vdW) crystals, including the prominent dimensionality effect and unprecedented magnetic field control of the Curie temperature in the nearly-ideal 2D Heisenberg ferromagnet. Significant fundamental physics in 2D magnetism and the corresponding exotic phenomena we observed will be expounded. Updated research on the complex magnon scatterings, material level engineering of 2D magnetism, and the development of novel concept of spintronic devices will be further discussed. Finally, I will envision the possible directions towards advancing 2D magnets for practical spintronic applications.

5:20pm **2D+EM+MN+NS-ThA10 Spectroscopic Evidence of Pair-mediated Bosonic Modes in Superconductor FeSe/SrTiO<sub>3</sub>(100) Film**, *Minjun Lee*, Seoul National University, Republic of Korea; *M. Oh, H. Jeon, S. Yi, I. Zoh*, Seoul National University, Republic of Korea; *C. Zhang*, Seoul National University, Republic of Korea; *J. Chae, Y. Kuk*, Center for Quantum Nanoscience, Institute for Basic Science, Republic of Korea

Single layer FeSe on SrTiO<sub>3</sub>(100) is atypical but noticed system in superconductivity. This has unique properties due to the substrate phonon. Unlike other bulk systems, the presence of the interface allows the substrate phonons to affect the superconducting layer. We have investigated substrate phonon effects on superconducting FeSe layer by using scanning tunneling spectroscopy and Eliashberg theory. We were able to measure acoustic, optical and substrate phonons in  $d^2I/dV^2$  spectroscopy. We found these phonon modes attribute to the pairing of electrons in this superconducting layer. These results are analyzed by Eliashberg model and we will discuss the coupling strength of these bosonic features. We have found that the substrate phonon has major contribution to increase the transition temperature of this system.

## MEMS and NEMS Group

### Room 202B - Session MN+2D+AN+NS-ThA

#### Nonlinear and Thermal Resonators

**Moderators:** Meredith Metzler, University of Pennsylvania, Christian Zorman, Case Western Reserve University

2:20pm **MN+2D+AN+NS-ThA1 Embracing Nonlinearity and Thermal Fluctuations in Nanomechanics**, *D. Lopez, David Czaplewski, C. Chen*, Argonne National Laboratory; *D. Zanette*, Centro Atomico Bariloche, Argentina; *S. Shaw*, Michigan State Univrsity **INVITED**

The field of micro-mechanics is now a well-established engineering domain with demonstrated impact in fundamental science and product development. Unfortunately, as the dimensions of the devices are reduced from the micro- to the nano-scale, the direct scaling of the fundamentals principles and fabrication processes cease to work. When going from micro- to nano-mechanical systems, MEMS to NEMS, the devices linear dynamic range can be reduced to the point where the amplitudes needed for lineal response are below the noise level and, as a consequence, operation in the nonlinear regime is unavoidable. Furthermore, thermal fluctuations and fluctuation-induced forces become relatively stronger causing significant changes in their dynamic response and on the manner in which they interact with the surrounding environment. This combination of nonlinear dynamics and high sensitivity to fluctuations has been seen as a deleterious combination for the advance of nano mechanical devices.

Rather than continuing to struggle to avoid these phenomena, it is of interest to consider how micro/nanosystem might effectively capitalize on

this nonlinear fluctuating response. In this talk, I will demonstrate that nonlinearity offers unique possibilities for the controlled response of micro and nano mechanical devices and, thereby, a host of novel application opportunities. Examples of these opportunities include the development of compact frequency sources with low phase noise, the engineering of dissipation reservoirs to manipulate energy decay processes, and the enhancement of synchronization range between microscopic and macroscopic oscillators.

3:00pm **MN+2D+AN+NS-ThA3 Probing Ion Radiation Effects in Silicon Crystals by 3D Integrated Resonating Thin Diaphragms**, *Hailong Chen, H. Jia, V. Pashaei*, Case Western Reserve University; *W. Liao, C.N. Arutt, M.L. McCurdy*, Vanderbilt University; *P. Hung*, The Aerospace Corporation; *R.A. Reed, R.D. Schrimpf, M.L. Alles*, Vanderbilt University; *P.X.-L. Feng*, Case Western Reserve University

Space radiation (e.g., solar, galaxy) and man-made radiation environments (e.g., nuclear plant) can expose devices to radiation at doses that may lead to severe damage [1]. In recent decades, a large body of work has been performed to understand radiation effects on mainstream solid state electronic devices [1-3], in particular on MOS devices [2] and integrated circuits [3]. Lately, microelectromechanical systems (MEMS) have seen widespread adoption in consumer, military and aerospace products due to their small size, low power consumption, and in some cases, monolithic integration with electronics [4]. As such, the reliability of MEMS devices for many applications in relatively benign environments has been well established [5]. However, the study of impact on mechanical properties due to radiation-induced damages is an area where limited research has been conducted.

In this work, we report on experimental investigation of heavy ion radiation effects on mechanical properties of Si crystals, by exploiting a novel 3D scheme of using 5 vertically stacked micromachined vibrating Si diaphragms (2 mm × 2 mm × 2 μm) exposed to oxygen ions. Simulations find the stop range of oxygen ions in Si is 7.3 μm. A Pelletron system is employed to irradiate oxygen ions into the Si diaphragms (10.3MeV, with a dose of 5.6 × 10<sup>13</sup>/cm<sup>2</sup>). Before and after radiation, multimode resonances are characterized in vacuum by using an ultrasensitive optical interferometry system. We have observed that diaphragms D1 and D2, which oxygen ions are expected to pass completely through, present modest multimode redshifts ranging from 0.85 kHz to 1.67 kHz, and 0.85 kHz to 1.19 kHz, corresponding to an average fractional frequency shift of 10.5% and 7.0%, respectively. In contrast, for devices D3 and D4, in which most ions are expected to stop, each resonance peak shifts much more dramatically, with a frequency shift of 27.3% and 20.4%. We attribute these large shifts to the very large capture area of the diaphragms, the very heavy and energetic oxygen ions, and high ion dose. Device D5 shows minimal frequency shifts among the five diaphragms because few oxygen ions reach and interact with this device layer. The diaphragm stack exhibits outstanding capability for probing radiation damages in MEMS, not only able to capture the radiation events obviously, but also help analyze different amount and types of damages induced in each stacking layer.

[1] L. Gregory, *et al.*, Proc. IEEE. **62**, 1974. [2] J. R. Srouf, *et al.*, Proc. IEEE. **76**, 1988. [3] H. L. Hughes, *et al.*, IEEE Trans. Nucl. Sci. **50**, 2003. [4] N. Arutt, *et al.*, Semicond. Sci. Technol. **32**, 2017. [5] H. R. Shea, Proc. SPIE. **7928**, 2011.

3:20pm **MN+2D+AN+NS-ThA4 An Array of Thermally-actuated Nanoresonators for Real-time Mass Spectrometry**, *Martial Defoort, M. Sansa, M. Gély, G. Jourdan, S. Hentz*, CEA/LETI-University Grenoble Alpes, France

Micro/Nano-ElectroMechanical Systems (M/NEMS) have attracted much attention in the last years in the mass spectrometry field. They feature high sensitivity, charge independent and single particle detection capabilities, in a mass range where conventional mass spectrometry struggles, hampering the analysis of large mass objects like protein complexes or viruses [1-4].

In general the size and mass of the device defines the size and mass ranges of the particles to measure for frequency tracking and point mass approximation purposes. However, as many silicon M/NEMS are electrostatically actuated, the gap between the driving electrode and the resonator becomes a critical parameter. While for many applications this gap should be as small as possible for high efficiency actuation and high signal-to-noise ratio, a particle landing within the gap results in a catastrophic failure of the device through electrical short-circuit or mechanical anchoring.

We present a new actuation scheme for doubly-clamped beams which relies on the thermal expansion of nano-actuators in silicon due to Joule

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heating, located close to the anchor of the resonator (Fig. 1), that we demonstrate to work in an array of 20 NEMS (Fig. 2). Unlike some thermoelastic actuation schemes [5], the technique we propose does not require an additional layer (of, for example, a metal) and is readily CMOS-compatible. Because of their small size and thermal capacity, the thermal time constant of the actuators is small enough to drive the resonator up to several 100's MHz with large efficiency and to actuate the two first flexural modes of the same device simultaneously, which is required for single particle mass sensing. The detection scheme uses the piezoresistive gauges located on the other end of the beam, as previously presented [6]. We compare the performance of this actuation technique with a standard electrostatic scheme both on the same array and demonstrate the thermal actuation does not affect the level of frequency fluctuations limiting the device mass resolution (Fig. 3).

1. Hanay *et al*, nature nanotechnology 2012.
2. Sage *et al*, nature communications 2015.
3. Sage *et al*, Arxiv 2017.
4. Dominguez-Medina *et al*, Arxiv 2018.
5. Mo Li *et al*, nature nanotechnology 2007.

6. Mile *et al*, nanotechnology 2010.

4:00pm **MN+2D+AN+NS-ThA6 Nonlinear and Noise Induced Dynamics of High Q Nanomechanical Resonators**, *Jana Huber, E.M. Weig*, University of Konstanz, Germany

**INVITED**

Doubly-clamped pre-stressed silicon nitride string resonators excel as high Q nanomechanical systems enabling room temperature quality factors of several 100,000 in the 10 MHz eigenfrequency range when operated under vacuum conditions. To retain the high mechanical quality factor, dielectric transduction is implemented as an all-electrical control scheme avoiding the metallization of the string. To this end, the string is exposed to an inhomogeneous electric field created between adjacent electrodes. The resulting gradient field provides an ideal platform for actuation, displacement detection, frequency tuning as well as strong mode coupling between the in- and out-of-plane modes of the string.

Here we focus on the nonlinear dynamics of the string subject to a strong drive. As a result of the high quality factor, cubic as well as higher order nonlinearities are observed. In the presence of thermal fluctuations, satellite resonances arise which enable deep insights into fundamental properties of the system.

4:40pm **MN+2D+AN+NS-ThA8 A Buckling-based, DC Controlled, Non-volatile Nanoelectromechanical Logic Memory**, *S.O. Erbil, Utku Hatipoğlu*, Bilkent University, Turkey; *C. Yanik*, Sabancı University; *M. Ghavami, M.S. Hanay*, Bilkent University, Turkey

Here, we demonstrate a buckling based, nanoelectromechanical logic bit with high controllability and low logic input voltage. The device consists of a slender beam to store information through its buckling direction and a comb-drive structure for initiating buckling electrostatically. When an actuation voltage is applied to the fingers of the comb-drive structure, an axial compressive force is applied to the suspended slender beam which is connected to an anchor from the opposite end. Applied axial force creates a compressive stress on the slender beam which leads to buckling after a critical load. Buckling direction can be controlled (left/right) by changing the applied side-gate control voltages. The capacitive attraction force generated between the beam and the activated electrode controls the direction of the buckling. Control voltage acts as the logic input for writing information and it is only required just before the application of the axial load, so that the beam can be preloaded to the target direction. Lateral deformations as large as 10% of the beam length can be achieved.

Once the beam is buckled to the desired direction, the removal of the guidance voltage does not affect the buckling state of the beam, which indicates successful non-volatile information storage. Moreover, by altering the voltage difference created in the comb-drive structure, buckling amount can be controlled very precisely. Control voltages as low as 0.5V are demonstrated for storing information. The device is fabricated from an SOI wafer by using electron beam lithography, metal deposition and plasma / HF etching techniques. The dimensions of the slender beam are 150nm x 250nm x 40µm for the width, thickness and length respectively. Several videos demonstrating dynamically controlled electrostatic buckling have been recorded during the experiments. The nanoelectromechanical logic memory demonstrated here is scalable since its operation does not require any high-end electronic instruments such as function generators, and can be accomplished by simply using DC power sources. To readout the

state of the beam all-electronically, the device is capacitively coupled to a microwave resonator. The changes in the frequency shows clear transitions between buckled and straight states.

It is possible to build two-bit mechanical logic gates and more involved logic units by using proposed nanoelectromechanical logic bit. As a further matter, precise control of the buckling in nanoscale can be very promising for demonstrating the interconnection between information science and thermodynamics.

## Nanometer-scale Science and Technology Division Room 102B - Session NS+2D+AS+MN+PC-ThA

### SPM – Probing Electronic and Transport Properties

**Moderators:** Ondrej Dyckoe, Oak Ridge National Laboratory, Sergei Kalinin, Oak Ridge National Laboratory, Indira Seshadri, IBM Research Division, Albany, NY

2:20pm **NS+2D+AS+MN+PC-ThA1 Imaging Currents in Two-dimensional Quantum Materials**, *Katja Nowack*, Cornell University

**INVITED**

Magnetic imaging is uniquely suited to the non-invasive imaging of current densities, particularly in two-dimensional devices. In this talk, I will showcase this approach by discussing measurements on HgTe quantum well devices in the quantum spin Hall (QSH) regime. In a nutshell, we scan a superconducting quantum interference device (SQUID) to obtain maps of the magnetic field produced by the current flowing in a device. From the magnetic image we reconstruct a two-dimensional current distribution with a spatial resolution on the micron scale. This allows us to directly visualize that most of the current is carried by the edges of the quantum well devices when tuned into their insulating gaps - a key feature of the QSH state. I will both discuss routes towards improving the spatial resolution of our measurements to sub-micron length scales through a combination of improved image reconstruction and smaller sensor sizes.

3:00pm **NS+2D+AS+MN+PC-ThA3 Side-gate Construct for Probing Active Energy Levels in Electron Transport through a Solid-state Surface-bound Protein Monolayer**, *Sidney Cohen, B. Kayser, C. Gua, M. Sheves, I. Pecht, D. Cahen*, Weizmann Institute of Science, Israel

Electron transport studies provide an excellent platform to deduce electronic structure in molecular electronics studies, enabling control and understanding of the pathways and mechanisms involved. Due to their complexity, proteins are used only infrequently in this context, despite convenient properties such as selective binding, self-assembly, light sensitivity, and the possibility to (bio) chemically tailor properties. Here, we study electron transport in monolayer films of Azurin, using a 3-electrode configuration with a novel side-gate. The source and drain are gold substrate and conductive atomic force microscope (C-AFM) probe, respectively. The measuring devices were prepared in a two-step electron beam lithography process, whereby interdigitated drain and gate electrodes with separation of 80 nanometers are patterned from macroscopic electrodes, the latter formed optically on a silicon oxide substrate. The gold electrodes are patterned with the gate elevated by 20 nm for improved coupling with the drain. After deposition of the Azurin monolayer on this structure, the carrier chip was wire-bonded for insertion into the AFM. Azurin was incorporated in the device both as copper-containing holo-Azurin, and as apo-Azurin with the Cu ion removed. Stability of source-drain vs.  $V_{\text{source-drain}}$  curves, as well as gate-drain leakage were monitored for validity.  $I_{\text{source-drain}}$  vs.  $V_{\text{source-drain}}$  curves were acquired at different gate voltages, and  $I_{\text{source-drain}}$  at 0  $V_{\text{source-drain}}$  was measured while sweeping  $V_{\text{gate}}$  in both polarities. Asymmetry of current onset for opposing gate biases points to a low-lying LUMO transport level for holo-Azurin. For apo-Azurin this level is shifted to higher values and hence inaccessible. Semi-quantitative location of the tail of this LUMO, as well as value of gate coupling were estimated by changing the work function of the drain electrode, i.e. C-AFM probe, from Pt ( $\phi = -5.3$  eV) to Au ( $\phi = -4.9$  eV). The observations can be rationalized by considering previous electrochemical and theoretical studies.



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3:20pm **NS+2D+AS+MN+PC-ThA4 Adding Electrons One at a Time to Electrostatically Confined Graphene Quantum Dots**, *Daniel Walkup, C. Gutierrez, F. Ghahari*, National Institute of Standards and Technology (NIST)/ University of Maryland, College Park; *C. Lewandowski*, MIT; *J. Rodriguez-Nieva*, Harvard University; *T. Taniguchi, K. Watanabe*, National Institute for Materials Science (NIMS), Japan; *L. Levitov*, MIT; *N.B. Zhitenev, J.A. Stroscio*, National Institute of Standards and Technology (NIST)

The Coulomb blockade of adding charges to isolated metallic systems is one of the most characteristic phenomena of quantum dots (QDs). Here, we created circular graphene QDs in a backgated graphene-hexagonal boron nitride (hBN) device by locally ionizing defects in the hBN layer, using the electric field from the tip of a scanning tunneling microscope (STM). Scanning tunneling spectroscopy (STS) enables us to image the local density of states outside and within these circular graphene resonators. At weak magnetic fields, confinement of graphene electrons is poor and Coulomb blockade is not observed. At higher fields, however, the graphene electrons form quantized Landau levels (LLs) separated by energy gaps. In the area of the QD, the LLs are bent by the electrostatic potential creating metallic (compressible) rings where a LL crosses the Fermi energy, separated by circular insulating barriers (incompressible strips), which isolate the dot from the graphene and enable the onset of Coulomb blockade. Tunneling  $dI/dV$  spectra inside the QD reveal a series of Coulomb blockade peaks, which shift as a function of back gate voltage. In the plane defined by gate voltage and sample bias, these peaks form Coulomb lines, whose slope is governed by the relative capacitances between the dot, tip, gate, and sample bias electrodes, and whose relative offsets reveal the addition spectrum of the quantum dot. A characteristic feature of the Coulomb blockade in these systems is the presence of different families of charging lines, one for each LL, which intersect each other and experience avoided crossings. The avoidance pattern of these anticrossings is novel: at the strongest fields, it somewhat resembles the predictions of simple models of electrostatically-coupled QDs, but at weaker fields it diverges very strikingly, and new modeling is needed to reproduce it. This avoidance pattern reflects the interaction of electrons in different LLs, occupying different parts of the QD, and is tunable via the magnetic field and gate voltage. By moving the STM tip, we can tune the tip-dot capacitance, and tunnel into different parts of the dot, enabling a full characterization of the anticrossings in these novel electronic nanostructures.

4:00pm **NS+2D+AS+MN+PC-ThA6 Bulk and Surface Contribution to the Charge and Spin Transport in Topological Insulators Observed with a Four-Probe Scanning Tunneling Microscope**, *Wonhee Ko, G.D. Nguyen*, Oak Ridge National Laboratory; *H. Kim, J.S. Kim*, Pohang University of Science and Technology, Republic of Korea; *A.-P. Li*, Oak Ridge National Laboratory

Topological insulators are fascinating materials for future electronics because of its superior charge and spin transport characteristics stemming from their topological nature. However, topological insulators realized in actual materials have both bulk and surface carriers, where the former significantly hampers the topological transport of the later. In this talk, we utilize four-probe scanning tunneling microscope to investigate bulk and surface contribution to the charge and spin transport in bulk-insulating topological insulator  $\text{Bi}_2\text{Te}_2\text{Se}$ . The relative contribution of bulk and surface was varied by changing temperature and transport area, which was measured by variable probe-spacing spectroscopy. The surface dominant regime was already reached at 82 K, where the sample exhibited superior transport properties such as a large surface mobility and high spin polarization. At this regime, the contact to external probes also transforms from Schottky to Ohmic junction. Our result indicates that controlling bulk and surface contribution to the transport is crucial for realizing topological devices.

4:20pm **NS+2D+AS+MN+PC-ThA7 Modulation of Single-Walled Carbon Nanotube Electronic Structure by External Electronic Perturbations: Scanning Tunneling Spectroscopy and Density Functional Theory**, *Benjamin Taber<sup>1</sup>, G.V. Nazin*, University of Oregon

Understanding the local impact of environmental electronic perturbations on the local density of states (LDOS) of single-walled carbon nanotubes (CNTs) is critical for developing CNT-based devices. We present scanning tunneling microscopy and spectroscopy (STM/STS) investigations of CNTs adsorbed on both a metal, Au(111), and a dielectric, monolayer RbI on Au(111), serving as models for stronger and weaker electrostatic interactions, respectively. In both cases, STS revealed modulations in the CNT LDOS corresponding to features in the underlying material. We then

corroborate our STM/STS results with density functional theory calculations of the electronic structure of semiconducting CNTs in the presence and absence of an external dipole (a pair of opposite charges).

DFT-calculated CNT LDOS quantitatively matched STM/STS results, providing key insight in to the local impact external charges have on CNT electronic structure.

4:40pm **NS+2D+AS+MN+PC-ThA8 Single Charge and Exciton Dynamics probed on the Molecular Scale**, *Anna Rosławska, P. Merino, C. Grosse, C.C. Leon, O. Gunnarsson, M. Etzkorn, K. Kuhnke, K. Kern*, Max Planck Institute for Solid State Research, Germany

The performance of organic optoelectronic devices depends on the dynamics of charges and excitons (electron-hole pairs). The relevant processes have been mostly studied by time-resolved techniques with a spatial resolution limited by optical diffraction. In order to overcome this limit, a nanoscale scanning probe approach that enables addressing individual light emitters is preferred. Here we introduce time-resolved scanning tunneling microscopy-induced luminescence (TR-STML) and use it to explore locally the single charge and single exciton regime. The excitonic light originates from structural defects in  $\text{C}_{60}$  thin films on Au(111) that act as charge and exciton traps. Such a defect is a single photon emitter, whose spectrum has a sharp electron-hole recombination feature [1,2]. By measuring the time-resolved electroluminescence due to individual injected charges, it is possible to analyze the formation and recombination processes of single excitons and determine their characteristic time constants[3].

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5:00pm **NS+2D+AS+MN+PC-ThA9 Microscopic Understanding of the Temperature-dependent Carrier Transport in Ge Nano - Crystal s Films**, *Dan Shan*, Yangzhou Polytechnic Institute, China; *J. Xu*, Nanjing University, China

Silica-based semiconductor nano-crystals have attracted much interest in recent years due to their possible applications in many kinds of nano-electronic and optoelectronic devices. Compared with Si, Ge has larger electron and hole mobility. Furthermore, Ge has a narrower band-gap and high phonon responsivity in the near-infrared region, so it is suited to many near-infrared applications. In order to further improve the device performance, detailed knowledge of transport mechanisms across these nano-crystals becomes necessary and is considered indispensable.

In this work, hydrogenated amorphous germanium films were prepared by a plasma enhanced chemical vapor deposition technique. Ge nano-crystals (Ge NCs) films were obtained by thermal annealing the as-deposited samples. P-type behavior in Ge NCs films without any external doping is attributed to the holes accumulation caused by acceptor-like surface states. It can be found that the dark conductivity and Hall mobility reach to as high as 25.4 S/cm and 182  $\text{cm}^2/\text{V}\cdot\text{s}$  in the Ge NCs film, which are much higher than the previously reported data. Carrier transport mechanisms of Ge NCs films were investigated by temperature-dependent Hall measurement. Three kinds of temperature-dependent conductivity behaviors, which exhibit the linear relationships of the  $\ln \sigma$  versus  $T^{-3/4}$ ,  $T^{-1/2}$  and  $T^{-1}$ , respectively, were observed in the temperature regions of 10-500 K. It can be confirmed that the thermal activation conduction in the extended states dominated the carrier transport process above 300 K (300-500 K). Below room temperature, the carrier transport process was dominated by the percolation-hopping conduction at 90-230 K and turned to Mott-VRH conduction when the temperature falling below 50 K (10-50 K).

Furthermore, the different scattering mechanisms in carrier transport process were found in different temperature regions, which were evaluated via temperature-dependent Hall mobilities. In the low temperature region (10-50 K), the carrier Hall mobility is almost temperature independence ( $\mu \sim T^0$ ), revealing the neutral impurities' scattering mechanism dominated the carrier transport process. When increasing the temperature (50-190 K), the carrier transport properties were controlled by the grain boundary scattering mechanism, where the carrier Hall mobility was increased with temperature and exhibited the thermally activated behavior. However, the relationship of  $\mu \sim T^{0.9}$  was observed above room temperature (300-500 K). It is suggested that the

<sup>1</sup> NSTD Postdoc Finalist

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carrier transport is dominated by a superposition of grain boundary scattering and acoustic phonon scattering within the high temperature region.

# Thursday Evening Poster Sessions, October 25, 2018

## MEMS and NEMS Group Room Hall B - Session MN-ThP

### MEMS and NEMS Group Poster Session

**MN-ThP1 The Ni-Co Micro-porous Array with High Dimensional Accuracy Control by Electroforming Process, YuHsin Lin, H.J. Wen, ITRC,NARL, Taiwan, Republic of China; C.J. Tsia, NCTU, Taiwan, Republic of China; M.-K. Wang, N.N. Chu, C.C. Chen, C.-N. Hsiao, ITRC,NARL, Taiwan, Republic of China**

In this project, the Ni-Co micro-porous array membrane for ultra-high sensitivity gas detector for nano particle distribution measurement is developed for cascade impactor application. The thick film lithography and electroforming technologies have been integrated, here. The dimension of micro-porous can be precisely controlled and reproducible. Finally, the micro-porous metal film will be integrated with base structure by laser welding technology. The component is used for cascade impactor equipment.

The fabrication process of Ni-Co micro-porous array membrane is used MEMS process. Here, the 6 inch silicon wafer as a substrate is used. The Cr/Au with 30/200nm thickness as a seedlayer is made by Sputter. The gold has good electrical conductivity to get well Ni-Co thickness uniformity at electroforming process. The AZ6112 photoresist is patterned on the seedlayer by lithography. The Cr/Au is etched to define a circle pattern. Then the thick photoresist SU8 pillar with 150 $\mu$ m thickness is fabricated at the center of the circle seedlayer pattern. The diameter of SU8 at the bottom is used to control the final diameter of Ni-Co porous. The Ni-Co membrane with 130 $\mu$ m thickness has been fabricated by electroforming process. Finally, the SU8 pillar is removed and the Ni-Co porous membrane is peel off from substrate. The Ni-Co micro-porous array membrane with good hole's dimension control have successful fabricated.

**Keywords:** Micro-porous, Electroforming, cascade impactor

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**MN-ThP2 Reactive Etching of AlGaN using BCl<sub>3</sub> and Ar/BCl<sub>3</sub>, Meng-Kun Wang, Y.-H. Lin, C.-N. Hsiao, C.C. Chen, J.S. Su, N.C. Chu, C.-T. Lee, ITRC,NARL, Taiwan, Republic of China**

In this paper, we study the self-limited reaction of Ar/BCl<sub>3</sub> and AlGaN. We performed AlGaN surface oxidation reaction with oxygen ions before Ar/BCl<sub>3</sub> etching on the AlGaN surface, and used the same power of inductively coupled plasma (ICP), the same working pressure, and the same. The etching time was compared to the difference in etching rate of AlGaN between Ar/BCl<sub>3</sub> and BCl<sub>3</sub>. And using Atomic force microscopy (AFM) and scanning electron microscopy (SEM) to observe the change and morphology of the surface roughness after etching. The results show that the mixed gas of Ar/BCl<sub>3</sub> has a faster etching rate, the etching rate is about 4.79 nm/min, and the etching rate of BCl<sub>3</sub> gas is slow, and the etching rate is about 0.90 nm/min.

**MN-ThP4 III-V Si Wafer Bonding using Silicon Oxide Interlayer, WoongSun Lim, S.H. Jung, Korea Advanced Nano Fab Center, Republic of Korea; S.Y. Hwang, Korea Advanced Nano Fab Center, Republic of Korea; G.Y. Yeom, Sungkyunkwan University, Republic of Korea**

In recently, the interests to integrate III-V based materials with Si can be divided into various application using the material advantages of combining III-V with Si. Therefore, Si wafer to III-V material wafer bonds were performed at low temperatures under 250 °C. The advantage of the low temperatures of these bonds was that wafers with common integrated circuit metals could withstand this temperature without degradation. Also, it is essential to study that low temperature bonding for heterogeneous wafers, because the higher temperature bonding may induce cracks, defects, bowing, and destruction by different thermal expansion coefficients of the heterogeneous wafers.

In this paper, we have investigated low-temperature direct bonding (<250°C) of SiO<sub>2</sub> by the surface activation method in plasma. In the method, Oxygen plasma treatment is used to make a clean surface which has strong bonding ability. The strength of Si oxide to Si oxide bonding prepared at room temperature by the method is equivalent to the bulk strength. Therefore, heating and pressure were applied to the wafers 20 minutes. Si oxide surfaces did not prove to bond spontaneously at room

temperature and the bond-strength started to increase only after annealing at about 200°C.

A field emission scanning electron microscopy (FE-SEM) was used to determine the excellent bonding quality of the interface of wafer to wafer bonding. Silicon oxide surface roughness was examined using atomic force microscopy (AFM), respectively. After bonding, the bonded interfaces were evaluated using infrared transmission imaging.

**MN-ThP5 Flexible Nanocomposite Sensors for Biomedical and Energy Harvesting Applications, A.K. Batra, Bir Bohara, Alabama A&M University; R. Currie, NASA**

Recently, an increase in demand for sensors for biomedical and ambient energy harvesting applications has led to the development of new hypersensitive smart materials. Biomedical sensors need to be able to be both lightweight, flexible and demonstrate high piezoresistive resolution. In order to meet the pressure sensor requirements for the next generation of prosthetics, efforts were made to develop and characterize multifunctional smart flexible nanocomposite films. The developed improved films could be used for both biomedical and energy harvesting applications.

Nanocomposites PVDF and P(VDF-TrFE) film-sensors were fabricated via embedding smart nanocomposites particles along with a variety of carbon nano-particles via the modified solution casting method. The fabrication methods involved in this study aimed at improving the sensitivity of sensors while maintaining flexibility and cost efficiency. The fabricated films were characterized by infrared and dielectric spectroscopy; performance of the sensors was determined via customized strain measurement and energy harvester testing system. Results obtained will be described along with unique features of system developed for performance determination. [This work is funded by NSF-HRD-1546965 grant.]

**MN-ThP6 Comparative Studies of Electrical Behavior of PLZT Thin Film Capacitors using Coplanar and Interplanar Configurations, Vaishali Batra, R. Paul, S. Kotru, The University of Alabama**

Lanthanum doped lead zirconate titanate (PLZT) is an interesting ferroelectric material which finds applications in optical MEMS & modulators/transducers, and smart sensors. Recent studies revealing the existence of bulk photovoltaic (PV) effect in this material thereby eliminating the need of fabricating a p-n junction, has generated curiosity among research community to explore this material for future energy/photo sensing applications. Various approaches are being explored to improve the PV output obtained from these devices.

In this work, capacitors with two electrode configurations viz. coplanar and interplanar were used to measure electrical properties. The capacitors were fabricated using thin films of Pb<sub>0.95</sub>La<sub>0.05</sub>Zr<sub>0.54</sub>Ti<sub>0.46</sub>O<sub>3</sub> (PLZT) and top and bottom electrodes of conducting materials. A chemical solution deposition method was used to prepare the films. The capacitance-voltage and polarization-voltage measurements demonstrated that the coplanar configuration shows higher capacitance, lower polarization, and higher coercive voltage as compared to the interplanar configuration. Further, the capacitors with coplanar configuration also demonstrated higher PV parameters, such as short circuit current density (J<sub>sc</sub>) and open circuit voltage (V<sub>oc</sub>). As an example, J<sub>sc</sub> of 1.86  $\mu$ A/cm<sup>2</sup> and V<sub>oc</sub> of -1.1 V were obtained using coplanar configuration with Au electrodes for unpoled devices. Poling showed an improvement in PV parameters for both the coplanar and interplanar configurations, with higher values obtained from the coplanar configuration. After poling, J<sub>sc</sub> of 1.32  $\mu$ A/cm<sup>2</sup> and V<sub>oc</sub> of -0.93 V for interplanar configuration, and J<sub>sc</sub> of 2.04  $\mu$ A/cm<sup>2</sup> and V<sub>oc</sub> of -2.01 V for coplanar configuration were obtained. These results suggest that coplanar configuration is better for measuring the PV properties of PLZT thin film based capacitor structures.

## 2D Materials Focus Topic

Room 201B - Session 2D+EM+MN+NS-FrM

### Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Xiang Zhang, University of California, Berkeley

8:20am **2D+EM+MN+NS-FrM1 Interfacial Strength and Surface Damage Characteristics of Two-dimensional h-BN, MoS<sub>2</sub> and Graphene**, *Frank DeRiio*, National Institute of Standards and Technology; *B.C. Tran Khac, K.H. Chung*, University of Ulsan, South Korea

Two-dimensional (2D) materials such as single- and multi-layer hexagonal boron nitride (h-BN), molybdenum disulfide (MoS<sub>2</sub>), and graphene have attracted intensive interest due to their remarkable material properties. In this study, the film-to-substrate interfacial strengths and surface damage characteristics of atomically-thin h-BN, MoS<sub>2</sub> and graphene were systematically investigated via atomic force microscopy (AFM)-based progressive-force and constant-force scratch tests and Raman spectroscopy. The film-to-substrate interfacial strengths of these atomically-thin films were assessed based on their critical forces (*i.e.*, normal force where the film was delaminated from the substrate) as determined from progressive-force scratch tests. The evolution of surface damage with respect to normal force was further investigated using constant-force tests. The results suggested three different steps in the evolution of surface damage. At relatively low normal force, no significant change in topography and friction force was observed, which points to elastic deformation in the scratched area. As normal force increased, the formation of defects in the film and plastic deformation in the substrate were noted. At this stage, although the films have not yet failed, their topography, friction force, crystalline quality, and mechanical strengths were affected, which notably degraded their tribological performance. At normal forces above the critical force, delamination of the film from the substrate occurred. The compressive strain-induced buckling in front of the

AFM tip was the primary source of mechanical instability. As the compressive strain increased, the atomic bonds were compressed, and eventually ruptured. As the number of layers increased, the tribological performance of h-BN, MoS<sub>2</sub>, and graphene were found to significantly improve due to an increase in the interfacial strengths and a decrease in the surface damage and friction force. In all, the findings on the distinctive surface damage characteristics and general failure mechanisms are useful for the design of reliable nanoscale protective and solid-lubricant coating layers based on these 2D materials.

9:00am **2D+EM+MN+NS-FrM3 Sequential Edge-epitaxy: Towards Two-dimensional Multi-junctions Heterostructures and Superlattices**, *Humberto Rodriguez Gutierrez*, University of South Florida **INVITED**

Atomically thin layers are known as two-dimensional (2D) materials and have attracted a growing attention due to their great potential as building blocks for a future generation of low-power and flexible 2D optoelectronic devices. Similar to the well-established 3D electronics, the development of functional 2D devices will depend on our ability to fabricate heterostructures and junctions where the optical and electronic properties of different compounds are brought together to create new functionalities. Vertical heterostructures can be produced by selective van der Waals stacking of different monolayers with distinct chemical composition. However, in-plane lateral heterostructures, where different materials are combined within a single 2D layer, have proven to be more challenging. During the formation of the hetero-junction, it is important to minimize the incorporation of undesired impurities and the formation of crystal defects at the junction that will impact the functionality of the 2D device. When fabricating periodic structures it is equally important to develop the ability to control the domain size of each material. In this talk, we will review different techniques that have been used to create 2D lateral heterostructures of transition metal dichalcogenide compounds. Emphasis will be made in our recently reported one-pot synthesis approach, using a single heterogeneous solid source, for the continuous fabrication of lateral multi-junction heterostructures of TMD monolayers. In this method, the heterojunctions are sequentially created by only changing the composition of the reactive gas environment in the presence of water vapor. This allows to selectively control the water-induced oxidation and volatilization of each transition metal precursors, as well as its nucleation on the substrate, leading to sequential edge-epitaxy of distinct TMDs. This simple method have proven to be effective for continuous growth of TMD-based multi-junction lateral heterostructures, including selenides, sulfides and ternary alloys. Basic devices with field effect transistor configuration were

fabricated to study the electrical behavior of these heterojunctions, their diode-like response, photo-response as a function of laser power as well as photovoltaic behavior of the heterojunctions will be discussed.

9:40am **2D+EM+MN+NS-FrM5 Interpretation of  $\pi$ -band Replicas Observed for Mono- and Multi-layer Graphene Grown on 4H SiC(0001)**, *T.B. Balasubramanian, M. Leandersson, J. Adell, C. Polley*, Lund University, Sweden; *Leif Johansson, R. Yakimova, C. Jacobi*, Linkoping University, Sweden

Graphene has made a major impact on physics due to its large variety of properties. The peculiar band structure of free standing graphene, showing linear dispersion and a Dirac point at the Fermi energy, makes it attractive for various applications. Large-scale epitaxial films have been grown on Si-terminated SiC substrates. However, the electronic structure is influenced when the graphene is laid upon a substrate whose lattice symmetry does not match that of graphene [1,2]. Six replicas oriented around each Dirac cone were observed already in the first ARPES experiments [1] of graphene grown on SiC(0001), and later reported [2] to have around 40 times lower intensity than a main Dirac cone. They were found to have the same relative separation and orientation as the rosette spots observed around the 0;th and 1x1 SiC and Graphene spots in the low energy electron diffraction (LEED) pattern and were explained [2] to have similar origin, *i.e.* to originate from photoelectron diffraction.

In two later ARPES investigations [3,4] additional weaker replicas were reported to exist along the  $\Gamma$ -K direction in the Brillouin zone of Graphene. One of them showed the existence [3] only for 1 ML but not 2 ML samples while the other reported [4] the existence in both 1 ML and 3 ML graphene samples. The origin of these replicas were in both cases attributed to a modulation of the ionic potential in the graphene layer/layers induced by the charge modulation of the carbon layer at the interface, *i.e.* the carbon buffer layer. Thus to an initial state effect instead of the earlier proposed final state effect. In both those experiments un-polarized HeI radiation was utilized, so the symmetry of the  $\pi$ -band replicas was not determined. We therefore investigated monolayer and multilayer graphene samples using linearly polarized synchrotron radiation, which allowed us to exploit the so called dark corridor [5] to directly determine the symmetry of the replica cones. Our ARPES data therefore clearly show the origin of these additional replicas observed using He-I radiation and moreover reveal the existence of some weaker replicas not earlier reported. An interpretation of our ARPES data in terms of final state photoelectron diffraction effects is shown to account for the location and symmetry of the  $\pi$ -band replicas observed.

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10:00am **2D+EM+MN+NS-FrM6 Effect of SiC(0001) Substrate Morphology and Termination on Multilayer Hexagonal Boron Nitride Epitaxy by Plasma-Enhanced CBE**, *Daniel J. Pennachio, N.S. Wilson, E.C. Young, A.P. McFadden, T.L. Brown-Heft*, University of California at Santa Barbara; *K.M. Daniels, R.L. Myers-Ward, D.K. Gaskill, C.R. Eddy, Jr.*, U.S. Naval Research Laboratory; *C.J. Palmström*, University of California at Santa Barbara

Despite the prevalent use of hexagonal boron nitride (hBN) in 2D devices as a gate dielectric, tunnel barrier, or substrate, the quality of hBN thin films are typically lacking relative to flakes exfoliated from bulk crystals. To address the challenges of hBN epitaxy, this work studies the growth of hBN on single-crystal epitaxial graphene on SiC(0001) via plasma-enhanced chemical beam epitaxy (PE-CBE). As PE-CBE is conducted in an ultra-high vacuum environment, hBN nucleation, composition, and morphology were able to be examined using a combination of *in-situ*, *in-vacuo*, and *ex-situ* characterization techniques to gain insight into the formation of high-quality hBN films and hBN/graphene heterostructures.

It was found that utilization of high growth temperature (>1400°C) and nitrogen plasma flux ( $5 \times 10^{-6}$  Torr background pressure) resulted in improved multilayer hBN film morphology over lower temperature (1300°C) depositions and CBE growths without nitrogen plasma flux. PE-CBE also produced more stoichiometric films than CBE without plasma at temperatures above 1400°C, as determined by *in-vacuo* X-ray photoelectron spectroscopy (XPS). *In-situ* reflection high energy electron diffraction (RHEED) showed streaky diffraction patterns persisting throughout several nanometers of PE-CBE hBN growth, indicative of a

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smooth, epitaxial film. Crystallinity and epitaxial arrangement of hBN nuclei were examined by *in-vacuo* and *ex-situ* scanning probe microscopy (SPM).

Scanning probe spectroscopy provided information on the electrical properties of the hBN films relative to bulk values.

The epitaxial alignment of the hBN/graphene/SiC(0001) heterostructure was studied by RHEED and by comparing nuclei edge alignment, as measured with SPM or scanning electron microscopy, to the substrate lattice orientation. It was found that the rotational alignment of the hBN nuclei depended on the substrate surface morphology. Nuclei on the (6V3×6V3)R30° SiC surface reconstruction, a graphene-like buffer layer, aligned directly to the buffer layer, while hBN nuclei on 4° off-cut epitaxial graphene substrates showed preferential alignment to substrate macrosteps rather than the graphene lattice. These ~25nm high macrosteps were then examined by cross-sectional transmission electron microscopy (TEM), which showed that the epitaxial graphene and hBN conformally blanketed the macrostep facets despite the macrostep's effect on nuclei orientation. The macrostep-directed nucleation outlined in this work provides a potential route to controlling the hBN/graphene rotational alignment during van der Waals epitaxy, an important variable for modulating electronic properties in this 2D system.

**10:20am 2D+EM+MN+NS-FrM7 Nanoelectromechanical Drumhead Resonators from 2D Material Bimorphs, Sun Phil Kim, J. Yu, E. Ertekin, A.M. van der Zande, University of Illinois at Urbana-Champaign**

Atomic membranes of monolayer 2D materials represent the ultimate limit in size of nanoelectromechanical systems. Yet, new properties and new functionality emerge by looking at the interface between layers in heterostructures of 2D materials. In this talk, we demonstrate the integration of 2D heterostructures as nanoelectromechanical systems and explore the competition between the mechanics of the ultrathin membrane and the incommensurate van der Waals interface. We fabricate electrically contacted, 5-6 μm circular drumheads of suspended heterostructure membranes of monolayer graphene on monolayer molybdenum disulfide (MoS<sub>2</sub>), which we call a 2D bimorph. We characterize the mechanical resonance through electrostatic actuation and laser interferometry detection. The 2D bimorphs have resonance frequencies of 5-20 MHz and quality factors of 50-700, comparable to resonators from monolayer or few layer 2D materials. The frequencies and eigenmode shape of the higher harmonics display split degenerate modes showing that the 2D bimorphs behave as membranes with asymmetric tension. The devices display dynamic ranges of 44 dB, but there is a strong dependence of the dissipation on the drive. Under electrostatic frequency tuning, devices display small tuning of ~ 20% compared with graphene resonators > 100%. In addition, the tuning shows a recoverable kink that deviates from the tensioned membrane model for atomic membranes, and corresponds with a changing in stress of 0.014 N/m. One model that would account for this tuning behavior is the onset of interlayer slip in the heterostructure, allowing the tension in the membrane to relax. Using density functional theory simulations, we find that the change in stress at the kink is much larger than the energy barrier for interlayer slip of 0.0001 N/m in a 2D heterostructure, but smaller than the energy barrier for an aligned bilayer of 0.034 N/m, suggesting local pinning effect at ripples or folds in the heterostructure. Finally, we observe an asymmetry in tuning of the full width half max that does not exist in monolayer materials. These findings demonstrate a new class of NEMS from 2D heterostructures and unravel the complex interaction and impact of membrane morphology, and interlayer adhesion and slip on the mechanics of incommensurate van der Waals interfaces.

**10:40am 2D+EM+MN+NS-FrM8 Atomically-precise Graphene Etch Masks for 3D Integrated Systems from 2D Material Heterostructures, Jangyup Son, University of Illinois at Urbana-Champaign; A.M. van der Zande, University of Illinois at Urbana-Champaign**

Atomically-precise fabrication methods are critical for the development of next-generation technologies in which electronic, photonic, and mechanical devices approach the atomic scale. In no area is this challenge more apparent than in nanoelectronics based on two-dimensional (2D) heterostructures, in which van der Waals (vdW) materials, such as graphene, hexagonal boron nitride (hBN), and transition metal dichalcogenides (TMDs), are integrated stacked to form functional electronic devices with nanometer thicknesses. A major challenge in the assembly of vdW heterostructure devices is the difficulty of patterning and individually connecting each molecular layer.

In this presentation, we demonstrate the use of graphene as a highly selective, atomically-thin etch mask and etch stop in van der Waals

heterostructures. We also show the advantages of graphene etch masks (GEM) through advanced device demonstrations. We demonstrate that most inorganic 2D materials, such as hBN, TMDs, and black phosphorus (BP), are efficiently etched away by exposing those to XeF<sub>2</sub> gas at room temperature. In contrast, instead of getting etched, atomically-thin monolayer graphene is chemically functionalized (*i.e.* fluorographene (FG)) under XeF<sub>2</sub> exposure due to the formation of *sp*<sup>3</sup> bonds by the addition of fluorine atoms onto the graphene surface. Based on this, we used exfoliated (and CVD) graphene layer as etch mask for patterning other 2D layers in micro (and macro) scale vdW heterostructures. We also demonstrate the use of this selective etching and GEM in mainly two different applications: 3D-integrated heterostructure devices with interlayer vias and suspended graphene mechanical resonators. First, we fabricate an electrical device having buried contacts in a 2D material heterostructure. Holes were etched through the top layer of hBN in an encapsulated BN-G-BN heterostructure to locally expose the buried graphene layer and contacts were fabricated by evaporating metal electrodes on the exposed graphene regions. The resulting encapsulated graphene device shows a low contact resistance of ~ 80 ohm·mm ( $n = -2 \times 10^{12} \text{ cm}^{-2}$ ) at room temperature, leading to high carrier mobility of ~ 140,000 cm<sup>2</sup>V<sup>-1</sup>s<sup>-1</sup>, which is comparable to the electrical properties of state-of-the-art edge contacted graphene devices. Second, we fabricate a suspended graphene membrane by vapor phase etching of a BP thin film supporting graphene. We show that the graphene membrane behaves as a nanomechanical resonator with a frequency of 5.24 MHz and quality factor of ~255, comparable to graphene NEMS prepared on conventional substrates.

**11:00am 2D+EM+MN+NS-FrM9 Insights into the O Atom Adsorption and O<sub>2</sub> Dissociation on Halogenated Graphene Surfaces, Reynaldo Geronia, University of the Philippines Diliman; A.A.B. Padama, University of the Philippines Los Baños, Philippines; J.D. Ocon, University of the Philippines Diliman, Philippines; P.-Y. A. Chuang, University of California, Merced**  
Oxygen reduction reaction (ORR) usually depends on precious metal-based catalysts like platinum and its alloys to facilitate its sluggish kinetics. The high cost of these materials however limits the employment of ORR-based technologies in commercial applications like fuel cells and metal-air batteries. Interestingly, recent works have demonstrated that doped metal-free carbon catalysts, such as graphene-based materials, can facilitate adsorption of ORR intermediate species [1]. This motivates us to investigate the interaction of oxygen atom and oxygen molecule on halogenated graphene systems.

In this work, we performed density functional theory (DFT) based calculations to investigate the stability of coplanar and non-coplanar halogen (X = F, Cl, Br, I) doped monovacant graphene systems. The stability of halogenated-graphene is strongly influenced by the size of halogen dopant as well as the geometry of the vacancy [2]. The calculated adsorption properties of atomic [3] and molecular oxygen on halogenated graphene systems, on the other hand, signifies the possibility of O<sub>2</sub> dissociation. We note that the dissociation of the molecule results to the distortion of the geometric structure of the substrate. This leads mostly to the formation of dangling and bridging C-O bonds along the edge of the graphene monovacancy which could have facilitated the dissociation of the molecule. Depending on the halogen, adsorption of oxygen can strengthen or weaken existing C-X bonds, due to differences between the abilities of oxygen and halogens to induce charge transfer and to participate in π bonding with carbon. These findings are expected to increase our understanding of novel graphene-based materials, which are currently being developed with the aim of reducing the use of noble metals as catalysts in fuel cells.

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- [2] R.M. Geronia, A.C. Serrao, A.A.B. Padama, J.D. Ocon, *ECS Trans.* 77 (2017) 607-620.
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# Friday Morning, October 26, 2018

## Nanometer-scale Science and Technology Division Room 102B - Session NS+AM+AS+MN+PC+PS+SS+TR-FrM

### SPM – Probing Chemical Reactions at the Nanoscale

**Moderators:** Phillip First, Georgia Institute of Technology, An-Ping Li, Oak Ridge National Laboratory

8:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM1 Using Self-Assembly to Engineer Electronic Properties in 1D and 2D Molecular Nanostructures, Michael F. Crommie**, University of California at Berkeley Physics Dept.

**INVITED**

Control of chemical reactions at surfaces has created new opportunities for on-surface synthesis of low-dimensional molecular nanostructures. By designing precursor molecules it is possible to engineer new bottom-up structures with atomic precision and predetermined electronic properties. We have used this technique to confirm recent predictions that quasi-1D graphene nanoribbons (GNRs) have well-defined electronic topology. This means that when “topologically non-trivial” GNRs are fused to “topologically trivial” GNRs then a singly-occupied, topologically-protected interface state occurs at the boundary between them. This has allowed us to engineer new GNRs with unique electronic structure. We have also engineered molecular precursors to control the behavior of 2D polymers. By tuning the coupling reaction between monomers it is possible to create 2D covalent organic frameworks (COFs) that exhibit novel electronic superlattice behavior.

9:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM3 Chemical and Electronic Structure of Aniline Films on Silica Surfaces, Christopher Goodwin**, University of Delaware; *A.J. Maynes*, Virginia Polytechnic Institute and State University; *Z.E. Voras*, University of Delaware; *S.A. Tenney*, Center for Functional Nanomaterials Brookhaven National Laboratory; *T.P. Beebe*, University of Delaware

The use of silica as a substrate for polyaniline is highly appealing since silica is a common component in photovoltaics. To this end we have developed a vacuum technique for the deposition and functionalization of silica with aniline, without the need for wet chemistry. To study the chemistry of the reaction, X-ray Photoelectron Spectroscopy (XPS), Time-of-Flight Secondary Ion Mass Spectroscopy (TOF-SIMS), and Atomic Force Microscopy (AFM), among other techniques, have been used. To determine the electronic structure of the resulting films, scanning tunneling microscopy and evaluation of valence band data collected by XPS was performed. By controlling the temperature of the gas-phase reaction, two states of aniline were found to exist on the silica surface. Our interest is in determining how the two states affect the electronic band structure of the surface.

9:20am **NS+AM+AS+MN+PC+PS+SS+TR-FrM4 Electric Field Driven Chemical Reaction of Individual Molecular Subunits by Scanning Tunneling Microscopy, Tomasz Michnowicz**, Max Planck Institute for Solid State Research, Germany, Deutschland; *B. Borca*, Max Planck Institute for Solid State Research, Germany; *R. Pétuya*, Donostia International Physics Centre, Spain; *M. Pristl*, *R. Gutzler*, *V. Schendel*, *I. Pentegov*, *U. Kraft*, *H. Klauk*, Max Planck Institute for Solid State Research, Germany; *P. Wahl*, University of St Andrews, UK; *A. Arnau*, Donostia International Physics Centre, Spain; *U. Schlickum*, *K. Kern*, Max Planck Institute for Solid State Research, Germany

Understanding of elementary steps and control in chemical reactions on the atomic scale might improve significantly their efficiency and applicability. Scanning tunneling microscopy (STM) allows both investigating and stimulating chemical reactions of individual organic subunits, for example via the tunneling current, electric field or a mechanical interaction. Here we present a study of an STM stimulated desulfurization process of the thiophene functional group embedded in a tetracenothiophene (TCT) molecule on a Cu(111) surface. Precise positioning and applying stimuli with the STM tip apex allows determination of a two-step process responsible for this chemical reaction. High resolution STM images, supported by the DFT calculations, help us to correlate the first reaction step to the breaking of one the carbon-sulfur bonds and the second to the breaking of the second carbon-sulfur bond. The latter reaction also results in a significant increase of the bond strength of the broken thiophene part to Cu surface atoms. The chemical reaction is triggered by positioning the tip apex above the thiophene part and applying a threshold voltage that depends linearly on the tip-molecule distance. This linear dependence is a hallmark of an electric field driven process. In addition, conduction measurements through single TCT molecules before and after the reaction have been performed. Compared to the intact molecule we observed a 50% increase of conductance after

the chemical reaction, which is in agreement with the finding of a much stronger bond formation between the molecule and Cu surface atoms.

9:40am **NS+AM+AS+MN+PC+PS+SS+TR-FrM5 Characterising Conjugated Polymers for Organic Electronics by High-resolution Scanning Probe Microscopy, Giovanni Costantini**, University of Warwick, UK

The structure of a conjugated polymer and its solid-state assembly are without a doubt the most important parameters determining its properties and performance in (opto)-electronic devices. A huge amount of research has been dedicated to tuning and understanding these parameters and their implications in the basic photophysics and charge transporting behaviour. The lack of reliable high-resolution analytical techniques constitutes however a major limitation, as it hampers a better understanding of both the polymerisation process and the formation of the functional thin films used in devices.

Here, by combining vacuum electrospray deposition and high-resolution scanning tunnelling microscopy (STM) we demonstrate the ability of imaging conjugated polymers with unprecedented detail, thereby unravelling structural and self-assembly characteristics that have so far been impossible to determine.

Applying this novel technique to prototypical DPP- and thiophenes-containing polymers, we show that sub-molecular resolution STM images allow us to precisely identify the monomer units and the solubilising alkyl side-chains in individual polymer strands. Based on this, it becomes possible to determine the molecular number distribution of the polymer by simply counting the repeat units. More importantly, we demonstrate that we can precisely determine the nature, locate the position, and ascertain the number of defects in the polymer backbone. This unique insight into the structure of conjugated polymers is not attainable by any other existing analytical technique and represents a fundamental contribution to the long-discussed issue of defects as a possible source of trap sites. Furthermore, the analysis of our high-resolution images, also reveals that the frequently assumed all-trans-conformation of the monomers in the polymer backbone is actually not observed, while demonstrating that the main driver for backbone conformation and hence polymer microstructure is the maximization of alkyl side-chain interdigitation.

10:00am **NS+AM+AS+MN+PC+PS+SS+TR-FrM6 Probing Electrical Degradation of Lithium Ion Battery Electrodes with Nanoscale Resolution, Seong Heon Kim**, Samsung Advanced Institute of Technology, Republic of Korea; *S.Y. Park*, *H. Jung*, Samsung Advanced Institute of Technology, Republic of Korea

The high performance of lithium-ion batteries (LIBs) is in increasing demand for a variety of applications in rapidly growing energy-related fields, including electric vehicles. To develop high-performance LIBs, it is necessary to thoroughly understand the degradation mechanism of LIB electrodes. The investigation of the electrical conductivity evolution during cycling can lead to a better understanding of the degradation mechanism in cathode and anode materials for Li-ion batteries. Here, we probed the electrical degradation of LIB electrodes with nanoscale resolution via quantitative and comparative scanning spreading resistance microscopy (SSRM). First, the electrical degradation of LiNi<sub>0.8</sub>Co<sub>0.15</sub>Al<sub>0.05</sub>O<sub>2</sub> (NCA) particles which are representative LIB cathode materials was studied [1].

After 300 charge/discharge cycles, stepwise-increasing resistance distributions toward the centers of the secondary particles were observed. These distributions correspond to the degenerated granular structures of the secondary particles caused by the formation of micro-cracks. Second, the electrical degradation of LIB anodes, the blended Si-C composites with graphite (Gr) particles, was investigated using SSRM [2]. From the SSRM measurements, it was obviously demonstrated that the electrical conductivity of the Si-C composite particles is considerably degraded by 300 cycles of charging and discharging, although the Gr particles maintain their conductivity. Our approach using SSRM techniques can be a good tool to study the electrical properties of various LIB electrode materials with nanoscale resolution.

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[2] S.H. Kim, Y.S. Kim, W.J. Baek, S. Heo, D.-J. Yun, S. Han, H. Jung, Nanoscale electrical degradation of silicon-carbon composite anode materials for lithium-ion batteries, Submitted.

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 Weiss, P.S.: NS+AM+MI+MN+SS+TR-TuA11, **13**  
 Wen, H.J.: MN-ThP1, **35**  
 Westly, D.A.: NS+2D+AN+MN+MP+SE-WeM2, **15**  
 Westover, T.:  
   NS+AN+EM+MI+MN+MP+PS+RM-ThM5, **28**  
 Whiteman, P.: NS+AM+MI+MN+SS+TR-TuA3, **12**  
 Wietstruk, M.: 2D+EM+MI+MN+NS+SS-ThM10, **24**  
 Wilkens, B.: BI+AS+IPF+MN-MoA10, **5**  
 Wilson, N.S.: 2D+EM+MN+NS-FrM6, **36**  
 Wong, M.: EM+MI+MN+NS-ThM5, **26**  
 Woolley, A.:  
   NS+AN+EM+MI+MN+MP+PS+RM-ThM5, **28**  
 Wu, J.: NS+2D+AN+EM+MN+MP+PC+RM-MoM11, **3**  
 — X —  
 Xiao, K.: 2D+MN+NS+SS-WeA10, **20**; 2D+MN+NS+SS-WeA9, **20**  
 Xiao, Z.: NS+AM+MI+MN+SS+TR-TuA9, **13**  
 Xu, J.: NS+2D+AS+MN+PC-ThA9, **33**  
 — Y —  
 Yakimova, R.: 2D+EM+MN+NS-FrM5, **36**  
 Yamaguchi, H.: NS+2D+AN+MN+MP+SE-WeM10, **16**  
 Yang, R.: MN+2D+AN+MP+NS-ThM11, **27**  
 Yang, Y.: 2D+EM+MI+MN+NS+SS-ThM11, **25**  
 Yanik, C.: MN+2D+AN+NS-ThA8, **32**  
 Yeh, K.L.: IPF+AS+BI+MN-TuM1, **7**  
 Yeh, P.: MN+NS+PS-WeM5, **14**  
 Yeom, G.Y.: MN-ThP4, **35**  
 Yi, G.-C.: 2D+EM+MI+MN+NS-TuA7, **10**  
 Yi, S.: 2D+EM+MN+NS-ThA10, **31**  
 Young, E.C.: 2D+EM+MN+NS-FrM6, **36**  
 Yu, J.: 2D+EM+MN+NS-FrM7, **37**  
 Yu, J.-S.: 2D+MN+NS+SS-WeA3, **19**; 2D+MN+NS+SS-WeA8, **20**  
 Yu, X.-Y.: BI+AS+IPF+MN-MoA8, **5**  
 Yurek, Q.: 2D+EM+MI+MN+NS-TuA11, **11**  
 — Z —  
 Zanette, D.: MN+2D+AN+NS-ThA1, **31**  
 Zehnder, A.T.: NS+2D+AN+MN+MP+SE-WeM2, **15**  
 Zhang, C.: 2D+EM+MN+NS-ThA10, **31**; 2D+MN+NS+SS-WeA10, **20**; NS+AN+EM+MN+MP+RM-TuM3, **8**  
 Zhang, X.: 2D+EM+MN+NS-ThA8, **31**; NS+2D+AN+EM+MN+MP+PC+RM-MoM11, **3**  
 Zhang, X.H.: 2D+EM+MI+MN+NS+SS-ThM11, **25**; 2D+MN+NS+SS-WeA12, **21**  
 Zhao, Y.: NS+2D+AN+EM+MN+MP+PC+RM-MoM4, **2**  
 Zhitenev, N.B.: NS+2D+AS+MN+PC-ThA4, **33**  
 Zhng, C.: 2D+MN+NS+SS-WeA9, **20**  
 Zhou, C.: 2D+EM+MI+MN+NS+SS-ThM2, **24**  
 Zhu, W.: NS+AN+EM+MN+MP+RM-TuM3, **8**  
 Zhu, Z.: NS+2D+AN+EM+MN+MP+PC+RM-MoM11, **3**  
 Zhu, Z.H.: BI+AS+IPF+MN-MoA8, **5**  
 Zoh, I.: 2D+EM+MN+NS-ThA10, **31**  
 Zorman, C.A.: MN+NS+PS-WeM3, **14**