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-MoM-1 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-MoM-3 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 (SnO_2) nanostructures were grown on a glass substrate by vapor-liquid-solid (VLS) process using a mixture of anhydrous tin (II) chloride ($SnCl_2$) and zinc chloride ($ZnCl_2$) powders. We demonstrate a new kind of single cell vapor deposition system to precisely control nanostructural morphology by changing the weight ratio of $SnCl_2$ and $ZnCl_2$ 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 SnO_2 nanostructures with different densities, sizes, and shapes can be achieved by adjusting the weight ratio of $SnCl_2$ and $ZnCl_2$. SnO_2 nanostructures with diameter ~20 nm and length ~100 nm showed ~85% sensitivity and 53 seconds of response time, whereas the nanorods with diameter ~100 nm and length ~ 1mm showed ~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 SnO_2 based sensors.

9:20am **NS+2D+AN+EM+MN+MP+PC+RM-MoM-4 Improving the Localized Surface Plasmonic Resonance Sensing Properties by Composite Metal/Dielectric Mixtures*, Steven Larson*[1]*, 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 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_{Ag})are shown to redshift with C_{Ag} until a composition threshold ($C_{Ag} \leq 90\%$) 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_{Ag} = 90 at.% 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-MoM-5 Improving the Selectivity of Tin (IV) Oxide Paper Based Gas Sensors with Plasma Surface Modification*, Kimberly Hiyoto,*** *E 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 ≥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 Ar/O_2 plasma modification of paper based, tin (IV) oxide (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 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-MoM-6 TiN@Si_3N_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 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

[1] **NSTD Student Award Finalist**

oxidation of the material and weaken its plasmonic response. The introduction of a secondary reactor with an input of SiH_4 as precursor gas leads to the formation of a Si_3N_4 coating. STEM and XPS analyses show that Si_3N_4 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_3N_4 by photo-induced reduction of an aqueous solution of chlorplatinic acid. After rinsing and centrifuging, the Pt/TiN@Si_3N_4 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-MoM-8 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-MoM-10 Templates for the Investigation of Size-Selected Nanocluster Networks**, ***Patrick Edwards,*** *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-MoM-11 High Performance Detection for X-ray and g -ray with $MAPbX_3$ 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 $MAPbX_3$ 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 $MAPbBr_3$ 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 $MAPbI_3$ single crystal, the p-n junction can be formed with doping of selenium atoms into $MAPbI_3$ single crystal.

With various temperature method, the 30mm×30mm×7mm $MAPbBr_3$ single perovskite crystal is fabricated. As the experimental results shown, almost all of the 100 keV x-ray photons are absorbed when the $MAPbBr_3$ SPC is 7mm thick. The detection sensitivity is as high as 305 µC $Gy_{air}^{-1}cm^{-2}$ 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/$MAPbBr_3$ PSC/C_{60}/PCBM/Ag has been fabricated with spin coating and sputtering methods. Although the dark current density can be reduced to 20 nA/cm^2 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 $MAPbI_3$ 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 $Gy_{air}^{-1}cm^{-2}$ and 41 mC $Gy_{air}^{-1}cm^{-2}$ 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.

Manufacturing Science and Technology Group
Room 202B - Session MS+MI+RM-TuM

IoT Session: Challenges of Neuromorphic Computing and Memristor Manufacturing (8:00-10:00 am)/Federal Funding Opportunities (11:40 am-12:20 pm)

Moderators: Christopher L. Hinkle, University of Texas at Dallas, Sean Jones, National Science Foundation, Alain C. Diebold, SUNY College of Nanoscale Science and Engineering

8:00am **MS+MI+RM-TuM-1 ReRAM – Fabrication, Characterization, and Radiation Effects***, **David Hughart**, R Jacobs-Gedrim, K Knisely, N Martinez, C James, B Draper, E Bielejec, G Vizkelethy, S Agarwal,* Sandia National Laboratories*; H Barnaby,* Arizona State University*; M Marinella,* Sandia National Laboratories **INVITED**

Resistive switching properties in transition metal oxides and other thin films have been an active area of research for their use in nonvolatile memory systems as Resistive Random Access Memory (ReRAM). ReRAM is a candidate for storage class memory technologies, and studies have also revealed a high degree of intrinsic radiation hardness making digital ReRAM a candidate for radiation-hardened memory applications. Analog ReRAM has also generated interest from the neuromorphic computing community for use as a weight in neural network hardware accelerators.

One of the manufacturing challenges for the valence change memory (VCM) type of ReRAM has been the development of substoichiometric switching layer films. Physical vapor deposited (PVD) substoichiometric TaO_x films are an attractive option for a VCM switching layer because they are complementary-metal-oxide-silicon (CMOS) compatible and are deposited at low temperatures. However, control of the oxygen partial pressure to produce substoichiometric TaO_x films cannot be directly achieved through flow control because the oxygen consumption by the Ta target and chamber surfaces is nonlinear as the chamber transitions from metal to insulator conditions. The oxygen partial pressure can be controlled using a feedback system, though feedback-assisted deposition techniques are difficult to regulate, making them ill-suited to production. One alternative to a feedback system is to deposit a higher stoichiometry TaO_x film, deposited in a more stable flow-partial pressure chamber regime, and use annealing to drive Ta into the film to achieve the desired stoichiometry. Here, we compare switching layers fabricated using both techniques, and discuss the relative merits of each technique. The devices are manufactured in crossbar arrays to be testable by automatic probers, enabling the collection of large scale yield and performance data sets across process splits.

Manufacturing improvements enabled fabrication of analog ReRAM with characteristics suitable for neuromorphic computing applications. The performance of a TaO_x ReRAM based hardware accelerator at image classification accuracy after training was evaluated. The classification accuracy showed little degradation in initial radiation tests, suggesting analog ReRAM may be suitable for neuromorphic computing applications in radiation environments as well.

Sandia National Laboratories is a multimission laboratory managed and operated by National Technology & Engineering Solutions of Sandia, LLC, a wholly owned subsidiary of Honeywell International Inc., for the U.S. Department of Energy's National Nuclear Security Administration under contract DE-NA0003525.

8:40am **MS+MI+RM-TuM-3 Memristive Synapses – Tuning Memristors for Performance and CMOS Integration***, **Nathaniel Cady**,* SUNY Polytechnic Institute **INVITED**

Neuromorphic computing systems can achieve learning and adaptation in both software and hardware. The human brain achieves these functions via modulation of synaptic connections between neurons. Memristors, which can be implemented as Resistive Random Access Memory (ReRAM), are a novel form of non-volatile memory expected to replace a variety of current memory technologies and enable the design of new circuit architectures. Memristors are a prime candidate for so-called "synaptic devices" to be used in neuromorphic hardware implementations. A variety of challenges persist, however, for integrating memristors with CMOS, as well as for tuning device electrical performance. My research group has developed a fully CMOS-compatible integration strategy for ReRAM-based memristors on a 300 mm wafer platform, which can be implemented in both front-end-of-line (FEOL) and back-end-of-line (BEOL) configurations. With regard to memristor performance, we are focusing on strategies to reduce stochastic behavior during both binary and analog device switching. This is a key metric for neuromorphic applications, as variability in device conductance state directly influences the ultimate number of levels (weights) that can be implemented per synapse. Using a two pronged approach, we have developed device operational parameters to maximize analog performance, while also tuning the ReRAM materials stack and processing conditions to reduce stochasticity and optimize switching parameters (forming, set, and reset).

9:20am **MS+MI+RM-TuM-5 Analog In-Memory Computing for Deep Neural Network Acceleration***, **Hsinyu Tsai**, S Ambrogio, P Narayanan, R Shelby, G Burr,* IBM Almaden Research Center **INVITED**

Neuromorphic computing represents a wide range of brain-inspired algorithms that can achieve various artificial intelligence (AI) tasks, such as classification and language translation. By taking design cues from the human brain, such hardware systems could potentially offer an intriguing Non-Von Neumann (Non-VN) computing paradigm supporting fault-tolerant, massively parallel, and energy-efficient computation.

In this presentation, we will focus on hardware acceleration of large Fully Connected (FC) DNNs in phase change memory (PCM) devices [1]. PCM device conductance can be modulated between the fully crystalline, low conductance, state and the fully amorphous state by applying voltage pulses to gradually increase the crystalline volume. This characteristic is crucial for memory-based AI hardware acceleration because synaptic weights can then be encoded in an analog fashion and be updated gradually during training [2,3]. Vector matrix multiplication can then be done by applying voltage pulses at one end of a memory crossbar array and accumulating charge at the other end. By designing the analog memory unit cell with a pair of PCM devices as the more significant weights and another pair of memory devices as the less significant weights, we achieved classification accuracies equivalent to a full software implementation for the MNIST handwritten digit recognition dataset [4]. The improved accuracy is a result of larger dynamic range, more accurate closed loop tuning of the more significant weights, better linearity and variation mitigation of the less significant weight update. We will discuss what this new design means for analog memory device requirements and how this generalizes to other deep learning problems.

1. G. W. Burr et al., "Experimental demonstration and tolerancing of a large-scale neural network (165,000 synapses), using phase-change memory as the synaptic weight element," IEDM Tech. Digest, 29.5 (2014).

2. S. Sidler et al., "Large-scale neural networks implemented with non-volatile memory as the synaptic weight element: impact of conductance response," ESSDERC Proc., 440 (2016).

3. T. Gokmen et al., "Acceleration of Deep Neural Network Training with Resistive Cross-Point Devices: Design Considerations," Frontiers in Neuroscience, 10 (2016).

4. S. Ambrogio et al., "Equivalent-Accuracy Accelerated Neural Network Training using Analog Memory," Nature, to appear (2018).

11:00am **MS+MI+RM-TuM-10 Computation Immersed in Memory: Integrating 3D vertical RRAM in the N3XT Architecture***, **Weier Wan**, W Hwang, H Li, T Wu, Y Malviya,* Stanford University*; M Aly,* Nanyang Technological University, Singapore*; S Mitra, H Wong,* Stanford University **INVITED**

The rise of data-abundant computing, where massive amount of data is processed in applications such as machine learning, computer vision and natural language processing, demands highly energy-effcient computing systems. However, the limited connectivity between separated logic and memory chips in conventional 2D system results in majority of program execution time and energy spent at memory access.The Nano-Engineered Computing Systems Technology (N3XT) [1] approach overcomes these memory bottlenecks by monolithically integrating interleaving layers of memory and logic on the same chip, and leveraging nano-scale interlayer vias (ILVs) to provide ultra-dense connectivity between logic and memory.

The metal oxide resistive switching memory (RRAM) [2] offers non-volatility, good scalability, and monolithic 3D integration, making it a good candidate as on-chip high-capacity main memory and storage in the N3XT system. Our experimentally calibrated studies show that a N3XT system with RRAM as digital storage and CNFET as logic devices could achieve 2-3 orders of magnitude improvement in energy efficiency (product of execution time and energy) in a wide range of applications (e.g. PageRank, deep neural network inference) compared to a conventional 2D system. Such 3D nano-system has also been experimentally demonstrated with

RRAM, CNFET and CMOS monolithically integrated to perform in-situ ambient gas classification [3] and hyper-dimensional computing [4].

Besides offering substantial benefits for conventional digital systems, the monolithic integration of RRAM and logic devices also enables “in-memory computing”, where computation is performed in the memory itself without explicitly moving data between memory and logic. Various types of in-memory computing operations could be performed using RRAM arrays, including analog multiply-accumulate and bit-wise logical operations. We perform system modeling that models program scheduling, communication and routing, and memory array and its peripheral circuits design on various operations to study their benefits and bottlenecks from application level. In particular we analyze the in-memory vector-matrix multiplication for deep neural network inference and bit-wise operations in 3D vertical-RRAM for hyper-dimensional computing. We show that with algorithm-architecture co-design, RRAM-based in-memory computing could further improve energy and area efficiency compared to digital implementation in a 3D monolithically integrated system.

[1] M.M.S. Aly et al., IEEE Computer, 2015. [2] H.-S P. Wong et al., Proc. IEEE, 2012. [3] M.M. Shulaker et al., Nature, 2017. [4] T. Wu et al., ISSCC, 2018.

11:40am **MS+MI+RM-TuM-12 Materials for the Second Quantum Revolution***, **Tomasz Durakiewicz**,* Los Alamos National Laboratory

Onset of the second quantum revolution is marked by proliferation of quantum technologies. Still mostly in the laboratory R&D phase, but likely to emerge soon as a growing sector of general consumer technology, quantum devices require constant supply of novel functional quantum materials. The current paradigm of meticulous long-term studies to understand fundamental properties in detail and be able to model them ab initio is unlikely to disappear; however, the rapid growth of technology may require modification of classical approach by accelerated discovery process aided by machine learning, data mining, and ability to model, synthesize and test novel materials quickly. In this presentation we will discuss opportunities and current developments in select classes of quantum materials, like low-dimensional materials, strongly correlated systems and topological insulators, and the role NSF plays in this rapidly growing area.

12:00pm **MS+MI+RM-TuM-13 SynBio(medicine): The Intersection Biomaterials and Living Systems***, **David Rampulla**,* National Institute of Health

The National Institute for Biomedical Imaging and Bioengineering (NIBIB) has long supported the development of biomaterials as platform technologies with broad biomedical application and has recently started a program in Synthetic Biology. This presentation will discuss the biomaterials portfolio at NIBIB with a specific focus on the use of synthetic biology approaches to engineer next generation materials for biomedicine. The talk will also highlight specific funding opportunities of interest and discuss some strategies for navigating the NIH application process.

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-TuM-1 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-TuM-3 Ultrafast Optical Pulse Shaping using Dielectric Metasurfaces***, **Amit Agrawal**, S Divitt, W Zhu, C Zhang, H 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-TuM-5 Single-Particle Nanophotonics and Materials Investigations with Optical Microresonator Spectrometers***, **Erik Horak**,* University of Wisconsin - Madison*; K Heylman, K Knapper, M Rea, F Pan, L Hogan, R 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_2 on Si toroidal resonators, we have developed an all-SiO_2 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-TuM-10 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 photonic and phononic crystals. We have designed and fabricated Si_3N_4 nanobeam optomechanical crystals with ~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 ~3 GHz-frequency slot-mode optomechanical crystals in Si_3N_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-TuM-12 Cold-atom based Sensors and Standards**, ***Stephen Eckel,*** *D Barker, J Fedchak, 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 produce 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.

Reconfigurable Materials and Devices for Neuromorphic Computing Focus Topic
Room 203A - Session RM+EM+NS-TuA
IoT Session: Reconfigurable Materials and Devices for Neuromorphic Computing

Moderators: Gina Adam, National Institute for R&D in Microtechnologies (IMT Bucharest), Brian Hoskins, National Institute of Standards and Technology (NIST)

2:20pm **RM+EM+NS-TuA-1 Non-volatile Memories for Neuromorphic Computing**, ***Alec Talin,*** Sandia National Laboratories **INVITED**

Inspired by the efficiency of the brain, CMOS-based neural architectures and memristors are being developed for pattern recognition and machine learning. However, the volatility, design complexity and high supply voltages for CMOS architectures, and the stochastic and energy-costly switching of memristors complicate the path to achieve the interconnectivity, information density, and energy efficiency of the brain using either approach. In my talk, I will review the latest advances in neuromorphic computing architectures based on deep neural networks implemented using CMOS and memristors and describe the challenges in achieving both high accuracy and energy efficiency using these devices. I will then discuss an alternative approach based on the non-volatile redox memory (NVRM): a device with a resistance switching mechanism fundamentally different from existing memristors, involving the reversible, electrochemical reduction/oxidation of a material to tune its electronic conductivity. The first type of NVRM that I will describe is based upon the intercalation of Li-ion dopants into a channel of $Li_{1-x}CoO_2$. This Li-ion synaptic transistor for analog computing (LISTA) switches at low voltage (mVs) and energy, displays hundreds of distinct, non-volatile conductance states within a 1V range, and achieves high classification accuracy when implemented in neural network simulations[1]. The second type of NVRM I will describe operates on a similar principle but is based on the polymer system PEDOT:PSS, and which we call the electrochemical neuromorphic organic device (ENODe) [2]. Plastic ENODes are fabricated on flexible substrates enabling the integration of neuromorphic functionality in stretchable electronic systems. Mechanical flexibility makes ENODes compatible with three-dimensional architectures, opening a path towards extreme interconnectivity comparable to the human brain.

1) E. J. Fuller et al., Advanced Materials 29, 1604310 2017.

(2) Y. B. van de Burgt et al., Nature Materials 16, 414 2017.

(3) S. Agarwal et al., IEEE 2017 Symposium on VLSI Technology Digest of Technical Papers, DOI: 10.23919/VLSIT.2017.7998164.

3:00pm **RM+EM+NS-TuA-3 Anionic and Protonic Transfer Materials for ReRAM and Neuromorphic Computing**, ***Jennifer Rupp,*** Massachusetts Institute of Technology **INVITED**

The next generation of information memories and neuromorphic computer logics in electronics rely largely on solving fundamental questions of mass and charge transport of oxygen ionic defects in materials and their structures. Here, understanding the defect kinetics in the solid state material building blocks and their interfaces with respect to lattice, charge carrier types and interfacial strains are the prerequisite to design new material properties beyond classic doping. Through this presentation basic theory1 and model experiments for solid state oxides their impedances and memristance2, electro-chemo-mechanics and lattice strain3-5 modulations is being discussed as a new route for tuning material and properties in ionic conducting oxide film structures up to new device prototypes based on resistive switching. Central are the making of new oxide film materials components, and manipulation of the charge carrier transfer and defect chemistry (based on ionic, electronic and protonic carriers)1-2, 5-6, which alter directly the resistive switching property and future computing performances. A careful study on the influence of microstructure and defect states vs. the materials` diffusion characteristics is in focus. For this, we suggest novel oxide heterostructure building blocks and show in-situ spectroscopic and microscopic techniques coupled with electrochemical micro-measurements to probe near order structural bond strength changes relative to ionic, protonic and electronic diffusion kinetics and the materials integration to new optimized device architectures and computing operation schemes.

1)Memristor Kinetics and Diffusion Characteristics for Mixed Anionic-Electronic SrTiO3-δ: The Memristor-based Cottrell Analysis Connecting Material to Device Performance F Messerschmitt, M Kubicek, S Schweiger, JLM Rupp Advanced Functional Materials, 24, 47, 7448 (2014) >

2)Uncovering Two Competing Switching Mechanisms for Epitaxial and Ultra-Thin Strontium Titanate-based Resistive Switching Bits M Kubicek, R Schmitt, F Messerschmitt, JLM Rupp ACS Nano 9, 11, 10737 (2015) >

3)Designing Strained Ionic Heterostructures for Resistive Swicthing Devices S Schweiger, R Pfenninger, W Bowman, U Aschauer, JLM Rupp Advanced Materials, (2016) >

4) The Effect of Mechanical Twisting on Oxygen Ionic Transport in Solid State Energy Conversion Membranes Y Shi, AH Bork, S Schweiger, JLM Rupp Nature Materials, 14, 721 (2015) >

5) A Micro-Dot Multilayer Oxide Device: Let's Tune the Strain-Ionic Transport Interaction S. Schweiger, M. Kubicek, F. Messerschmitt, C. Murer, J.L.M. Rupp ACS Nano, 8, 5, 5032 (2014) >

6) How does Moisture affect the Physical propert of Memristance for Anionic-Electronic Resistive Switching Memories? F Messerschmitt, M Kubicek, JLM Rupp Advanced Functional Materials, 25, 32, 5117 (2015) >

4:20pm **RM+EM+NS-TuA-7 Memristor Neural Networks for Brain-Inspired Computing**, ***Qiangfei Xia,*** University of Massachusetts Amherst **INVITED**

As CMOS scaling approaches its limits, it becomes more difficult to keep improving the speed-energy efficiency of traditional digital processors. To address this issue, computing systems augmented with emerging devices particularly memristors, offer an attractive solution. Memristors use conductance to represent analog or digital information. The dynamic nature of memristor with both long-term and short-term memories, together with its small effective size contributes to the energy efficiency in weight updating (training). The in-memory computing scheme in a crossbar breaks the 'von Neumann bottleneck' as the weights are stored locally in each device during computing. The read out (inference) is finished in one clock cycle regardless of the array size, offering massive parallelism and hence high throughput. The capability of using physical laws for computing in a crossbar enables direct interfacing with analog signals from sensors without energy- hungry analog/digital conversions.

We developed a Ta/hafnium oxide memristor with stable multilevel resistance, linear current voltage characteristics in chosen conductance ranges, in addition to high endurance and long retention. We further integrated the memristors with foundry-made transistors into large arrays. We demonstrated that the reconfigurable memristor networks are capable of analog vector matrix multiplication, and successfully implemented a number of important applications including signal processing, image compression and convolutional filtering. We also built a multilayer memristor neural network, with which we demonstrated in-situ and self-adaptive learning capability with the MNIST handwritten digit dataset. The successful demonstration of analog computing and in-situ online training suggests that the memristor neural network is a promising hardware technology for future computing.

5:00pm **RM+EM+NS-TuA-9 Indium Phosphide Synaptic Device on Silicon for Scalable Neuromorphic Computing**, ***Jun Tao****, D Sarkar, R Kapadia,* University of Southern California

Inspired by the superior capability of the brain, neuronal spiking, and synaptic behavior have been mimicked by the CMOS-based neuronal cell in hardware, which contains 6-12 transistors depending on specific functionality and the robustness of the design. However, the higher energy consumption and physical area have led researchers to look for architectures based on single device and novel materials.

In our work, utilizing thin-film vapor-liquid-solid growth method, we fabricated scalable Indium phosphide (InP) channel transistors directly on Si/SiO_2 wafer, which can emulate significant synaptic characteristics such as elasticity, short- and long-term plasticity, metaplasticity, spike number dependent plasticity and spike timing dependent plasticity, by modeling gate electrode as the pre-synaptic axon terminal, the drain electrode as the post-synaptic dendrite, and the gate oxide-semiconductor channel as the synapse junction, in which we also interpreted the FET channel conductance as the synaptic weight.

We also demonstrated that by controlling the charging and discharging of interfacial traps at the gate oxide-semiconductor stack, we can essentially engineer hysteresis of the synaptic device to customize the synapse behavior and modify the synapse weight non-linearly. It underpins optimal selectivity of signal transduction and satisfies the key neuromorphic architecture characteristic—training and learn. Tuning hysteresis in a family of transfer characteristics in spike timing dependent plasticity (STDP) emulation, we attain maximum potentiation (depression) for the minimum positive (negative) interval time, which gradually decays down to elasticity, as we expected, indicating the scalable InP channel transistors on silicon as promising devices and platform for neuromorphic computation.

5:20pm **RM+EM+NS-TuA-10 Ultra-low Power Microwave Oscillators based on Phase Change Oxides as Solid-State Neurons***, **Boyang Zhao**, J Ravichandran,* University of Southern California

Voltage or current controlled oscillators are well-established candidates for solid-state implementations of neurons. Metal to insulator transition (MIT) based phase change electrical oscillators are one of the many candidates for solid-state neurons, but current implementations are far from the ideal performance limits of energy and time necessary to induce the transition. We propose the use of nanoscale, epitaxial heterostructures of phase change oxides such as VO_2, NbO_2 and oxides with metallic conductivity as a fundamental unit of a low power electrical oscillator, capable of operating as neurons for neuromorphic computing architectures. Our simulations such that such oscillators can operate in the microwave regime and overcome many of the power consumption issues plagued by phase change electrical oscillators.

5:40pm **RM+EM+NS-TuA-11 Leveraging Nanodevice Volatility for Low Energy Computing Inspired from Nature***, **Alice Mizrahi,*** NIST/University of Maryland*; T Hirtzlin,* Centre de Nanosciences et Nanotechnologies*; B Hoskins,* NIST Center for Nanoscale Science and Technology*; A Fukushima,* AIST*; A Madhavan,* NIST Center for Nanoscale Science and Technology*; H Kubota, S Yuasa,* AIST*; N Zhitenev, J McClelland, M Stiles,* NIST Center for Nanoscale Science and Technology*; D Querlioz,* Centre de Nanosciences et Nanotechnologies, France*; J Grollier,* UMR CNRS/Thales **INVITED**

Artificial neural networks are performing tasks, such as image recognition and classification, that were thought only accessible to the brain. However, these algorithms run on traditional computers and consume orders of magnitude more energy more than the brain does at the same task. One promising path to reduce the energy consumption is to build dedicated hardware to perform cognitive tasks. Nanodevices are particularly interesting because they allow for complex functionality with low energy consumption and small size. I discuss two nanodevices. First, I focus on stochastic magnetic tunnel junctions, which can emulate the spike trains emitted by neurons with a switching rate that can be controlled by an input. Networks of these tunnel junctions can be combined with CMOS circuitry to implement population coding to build low power computing systems capable of processing sensory input and controlling output behavior. Second, I turn to different nanodevices, memristors, to implement a different type of computation occurring in nature: swarm intelligence. A broad class of algorithms inspired by the behavior of swarms have been proven successful at solving optimization problems (for example an ant colony can solve a maze). Networks of memristors combined with CMOS circuitry can perform swarm intelligence and find the shortest paths in mazes. These results are striking illustrations of how matching the functionalities of nanodevices with relevant properties of natural systems open the way to low power hardware implementations of difficult computing problems.

Reconfigurable Materials and Devices for Neuromorphic Computing Focus Topic
Room Hall B - Session RM-TuP

Reconfigurable Materials and Devices for Neuromorphic Computing Poster Session

RM-TuP-1 Selector-less Crossbar Array through Self-rectifying Characteristic of Pt/HfO_2/Ti Memristor, ***Yong Kim**, S Ryu, W Jeong,* Seoul National University of Science and Technology, Republic of Korea*; K Min,* Kookmin University, Republic of Korea*; B Choi,* Seoul National University of Science and Technology, Republic of Korea

DRAM and flash memory currently being used as working memory devices must be configured with transistors. For this reason, it has been reached the limits of scaling, power consumption and fabrication cost. In order to overcome these limits, next-generation memory devices have been developed and materials/device structures have been studied actively. Memristor could be used as a nonvolatile memory with simple crossbar array (CBA) structure. Although CBA structure is possible to innovatively overcome the scaling limits, it has major problem, so called sneak path current. It is caused by cross talking near the selected cell and typically solved by adding an additional selector device (e.g., diode, transistor, etc.). Recently, self-rectifying memristor could be enabled by bilayer stack, which could much simplifying the CBA structure: selector-less CBA. We fabricated the 10x10 and 30x30 CBA as selector-less memristor device using the potential barrier between each stack of the fabricated MIM structure.

In this study, we have acquired the self-rectifying characteristics for CBA structure using the Pt/HfO_2/Ti device. The device was fabricated 10x10 and 30x30 CBA patterned with 2 – 20 µm of electrode size. The top/bottom electrodes were deposited using electron beam evaporator and the dielectric material was deposited by atomic layer deposition (ALD). HfO_2 layer grown by ALD plays the role of switching layer in memristor. The thickness of the switching layer was quite thin, which eliminates the need for electroforming process. In addition, we obtained the self-rectifying characteristic that does not permit the fluent current conduction under negative bias through the potential barrier between Pt and HfO_2 layer.

As a result of electrical properties, this device follows an interface-type switching mechanism in which the current value decreased as the electrode size decreased. By inserting Al_2O_3 layer of 1 - 2nm, it was confirmed that switching occurs in HfO_2/Ti interface. The size of the formed conductive region was changed through the positive bias and the stability of the rectifying function was verified by applying the negative bias up to -3V. We confirmed the uniformity of memristor cells randomly chosen among 10x10 and 30x30 CBA and verified the device-to-device variability. Cycle-to-cycle variability was also obtained from these cells through a switching of more than 100 cycles. Finally, the AC measurement was applied to explore the possibility of fabricated device as a synaptic device.

RM-TuP-2 Electron Beam Induced Current Microscopy of Interfacial Barrier Effects in Al_2O_3/TiO_x Resistive Switches, ***Brian Hoskins,*** National Institute of Standards and Technology (NIST)*; G Adam,* National Institute for R&D in Microtechnologies (IMT Bucharest), Romania*; E Strelcov,* National Institute of Standards and Technology (NIST)/University of Maryland*; A Kolmakov, N Zhitenev,* National Institute of Standards and Technology (NIST)*; D Strukov,* University of California at Santa Barbara*; J McClelland,* National Institute of Standards and Technology (NIST)

Resistive switching devices (ReRAM) represent a broad class of two-terminal continuously tunable resistors including memristors, phase change memory (PCM), valence change memory (VCM), and electrochemical metallization cells (ECM). Though these devices, especially PCM, are increasingly being commercialized by industry for use in next generation memories, they are also all actively studied for use as synaptic weights in next generation hardware-accelerated neuromorphic networks.

We have previously investigated Electron Beam Induced Current Microscopy as a means of reliably characterizing resistive switches. In that investigation, we observed surprising electronic effects, such as internal secondary electron emission, in addition to more traditional electron-hole pair separation, and we broke those up into constituent currents based on their origin through Monte-Carlo modeling of the electron beam-matter interaction.

Now, armed with a new understanding of the physics of EBIC imaging, we study the impact of manufacturing variations on resistive switches by continuously tuning the thickness of an Al_2O_3 interfacial barrier. Shifts in the apparent ratios of internal secondary electron emission from the top electrode to the bottom electrode and vice versa appear to indicate a continuous tuning of the apparent filament diameter as both a function of the injected current and the interfacial barrier thickness. This yields an apparent reduction in the current density, the primary effect of which is a reduction in the device damage from forming and a suppression of parasitic leakage currents imaged in devices without interfacial barriers.

RM-TuP-3 Ion-insertion Electrodes for Brain Inspired Computing, ***Elliot Fuller***, Sandia National Laboratories*; S Keene,* Stanford University*; Z Wang,* University of Massachusetts Amherst*; S Agarwal, R Jacobs-Gedrim, J Niroula, C Bayley, U Sohi,* Sandia National Laboratories*; A Melianas, Y Tuchman,* Stanford University*; M Marinella,* Sandia National Laboratories*; J Yang,* University of Massachusetts Amherst*; A Salleo,* Stanford University*; A Talin,* Sandia National Laboratories

A major barrier to realizing neuromorphic hardware has been the development of analog memory with the programmability and impedance required for fully parallel computation and large scale integration. Existing resistive memory, i.e. phase change memory (PCM) and filament forming metal oxides (FFMO), suffer from non-linear programming that precludes parallel training operations. Furthermore, the devices are not capable of high impedance simultaneously with high accuracy and therefore suffer from circuit parasitics that limit parallel inference operations to less than 100x100 elements. Parallel operation of arrays larger than 1,000x1,000 elements is required for energy efficiency gains over CMOS.

To address these issues, ionic floating-gate memory (IFG) based upon ion-insertion electrodes and diffusive memristors was invented at Sandia National Laboratories. IFG is capable of fully parallel computation for both training and inference operations and can operate with both high accuracy and high impedance in order to realize arrays larger than 1,000x1,000 elements. Here, we demonstrate fully-parallel programming of prototype IFG arrays with vector-matrix multiplication (inference) and outer product update (training) operations. When scaled, IFG arrays are projected to operate with orders of magnitude lower energy consumption than PCM or FFMO and achieve ideal accuracy in neural networks. The key to IFG performance is the use of ion-insertion electrodes as a low-voltage, linearly programmable element[1, 2] and the use of a volatile, nano-electromechanical switch (diffusive memristor)[3] for array selectivity and cell retention. Here, I will discuss the physics and performance of these devices as well as the engineering and materials science challenges for fully integrating them into neuromorphic hardware.

[1] E. J. Fuller, F. E. Gabaly, F. Léonard, S. Agarwal, S. J. Plimpton, R. B. Jacobs-Gedrim*, et al.*, "Li-Ion Synaptic Transistor for Low Power Analog Computing," *Advanced Materials,* 2017

[2] Y. van de Burgt, E. Lubberman, E. J. Fuller, S. T. Keene, G. C. Faria, S. Agarwal*, et al.*, "A non-volatile organic electrochemical device as a low-voltage artificial synapse for neuromorphic computing," *Nature Materials,* 2017

[3] R. Midya, Z. Wang, J. Zhang, S. E. Savel'ev, C. Li, M. Rao*, et al.*, "Anatomy of Ag/Hafnia-Based Selectors with 1010 Nonlinearity," *Advanced Materials*, 2017

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-ThM-1 Femtosecond Laser Processing of Ceria-Based Micro Actuators***, **Jenny 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,* 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 ≈ 2 µm-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 × 0.5 mm in size. Finally, ≈ 1.2 mm long and ≈ 100 µm wide the double-clamped beams were cut from the membranes using a femtosecond (fs) laser, demonstrating an unharmful 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 ~0.3 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 ≈ 45 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.

8:20am **NS+AN+EM+MI+MN+MP+PS+RM-ThM-2 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 (≈ 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-ThM-3 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. & Fygenson, 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-ThM-5 Polymer Templated Annealing of DNA Patterned Gold Nanowires***, **Tyler Westover**, B Aryal, R 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-ThM-10 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 course 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-ThM-12 Three Dimensional Mesoporous Silicon 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 Ω·cm) was coated with about 22 nm silver film at 350 °C for 5~6 hours in a vacuum furnace (pressure < 3×10^{-7} 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_2O_2: 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 pore size. The aspect ratio of the silicon nanowire network can be controlled by the etching rate. The etching rate was roughly one µm/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-ThM-13 Enhancing Light Extraction from Free-standing InGaN/GaN light Emitters Using Bio-inspired Backside Surface Structuring**, *L Chan, C Pynn, S 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 = 170–2530 nm) and Cl_2/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.

Electronic Materials and Photonics Division
Room 101A - Session EM+2D+NS+PS+RM+TF-ThA

IoT Session: Flexible Electronics & Flash Networking Session

Moderators: Shalini Gupta, Northrop Grumman ES, Sang M. Han, University of New Mexico

2:20pm **EM+2D+NS+PS+RM+TF-ThA-1 Epitaxial Electrodeposition of Electronic and Photonic Materials onto Wafer-size Single Crystal Gold Foils for Flexible Electronics*, Jay Switzer,*** Missouri University of Science and Technology **INVITED**

Single-crystal silicon (Si) is the bedrock of semiconductor devices due to the high crystalline perfection that minimizes electron-hole recombination, and the dense SiO_x native oxide that minimizes surface states. There is interest in moving beyond the planar structure of conventional Si-based chips to produce flexible electronic devices such as wearable solar cells, sensors, and flexible displays. Most flexible electronic devices are based on polycrystalline materials that can have compromised performance due to electron-hole recombination at grain boundaries. In order to expand the palette of electronic materials beyond planar Si, there is a need for both an inexpensive substrate material for epitaxial growth, and an inexpensive and scalable processing method to produce epitaxial, grain-boundary-free films of metals, semiconductors, and optical materials. Recently, in our laboratory, we have developed a process for producing wafer-size, flexible, and transparent single-crystal Au foils by an electrochemical processing method.[1] Au is epitaxially electrodeposited onto Si using a very negative applied potential. An interfacial layer of SiO_x is then produced photoelectrochemically by lateral undergrowth. The Au foil is then removed by epitaxial lift-off following an HF etch. We will report on the electrodeposition of epitaxial films of metal oxide semiconductors such as Cu_2O and ZnO onto the highly-ordered and flexible Au foils. We will also present new, unpublished results in which we spin-coat epitaxial films of perovskites, such as $CsPbBr_3$, directly onto these Au foils and onto other single crystals.

Acknowledgement: This presentation is based on work supported by the U.S. Department of Energy, Office of Basic Sciences, Division of Materials Science and Engineering under grant No. DE-FG02-08ER46518.

[1] Mahenderkar N., Chen Q., Liu Y.-C., Duchild, A., Hofheins, S. Chason E., Switzer J (2017). Epitaxial lift-off of electrodeposited single-crystal gold foils for flexible electronics. Science, **355**, 1203-1206.

3:00pm **EM+2D+NS+PS+RM+TF-ThA-3 Flexible Electronic Devices Based on Two Dimensional Materials***, R Kim, N Glavin,* Air Force Research Laboratory*; R Rai, K Gliebe, M Beebe,* University of Dayton; Air Force Research Laboratory*; J Leem,* University of Illinois at Urbana-Champaign, Republic of Korea*; S Nam,* University of Illinois at Urbana-Champaign*; R Rao,* Air Force Research Laboratory*; **Christopher Muratore**,* University of Dayton

Low temperature synthesis of high quality 2D materials directly on flexible substrates remains a fundamental limitation towards realization of robust, strainable electronics possessing the unique physical properties of atomically thin structures. Here, we describe room temperature sputtering of uniform, stoichiometric amorphous MoS_2, WSe_2, and other transition metal dichalcogenides and subsequent large area (>2 cm^2) photonic crystallization to enable direct fabrication of two-dimensional material photodetectors on large area flexible PDMS substrates. Fundamentals of crystallization kinetics for different monolithic and heterostructured TMDs are examined to evaluate this new synthesis approach for affordable, wearable devices. The photodetectors demonstrate photocurrent magnitudes and response times comparable to those fabricated via CVD and exfoliated materials on rigid substrates and the performance is unaffected by strains exceeding 5%. Other devices and circuits fabricated from crystallized 2D TMDs deposited on large area flexible substrates are demonstrated.

3:20pm **EM+2D+NS+PS+RM+TF-ThA-4 Contact Resistances and Schottky Barrier Heights of Metal-SnS Interfaces***, **Jenifer Hajzus**, L Porter,* Carnegie Mellon University*; A Biacchi, S Le, C Richter, A Hight Walker,* National Institute of Standards and Technology (NIST)

Tin(II) sulfide (SnS) is a natively p-type, layered semiconductor that is of interest for two-dimensional and optoelectronic applications. Understanding the behavior of contacts to SnS is essential for its use in devices. In this work, contact metallizations with a range of work functions were characterized on both solution-synthesized, p-type SnS nanoribbons and electron-beam evaporated, polycrystalline SnS thin films. The structure and properties of electron-beam evaporated SnS films were dependent upon deposition temperature and post-deposition annealing. A deposition temperature of 300 °C followed by vacuum annealing at 300 °C resulted in p-type, orthorhombic SnS films. Specific contact resistances of Ti/Au, Ru/Au, Ni/Au, and Au contacts were measured on SnS films using circular transfer length method (CTLM) patterns prior to and after annealing the contacts at 350 ° C in argon. All metallizations on SnS thin films were ohmic prior to annealing. A trend of decreasing average specific contact resistance with increasing metal work function was observed for the as-deposited contacts. Annealed Ru/Au exhibited the lowest average specific contact resistance of ~1.9×10^{-3} Ω -cm^2. Contacts were additionally patterned onto individual, solution-synthesized SnS nanoribbons. In contrast to the behavior of contacts on electron-beam evaporated films, low work function metals (Cr/Au and Ti/Au) formed Schottky contacts on SnS nanoribbons, whereas higher work function metals (Ni/Au and Pd/Au) formed ohmic or semi-ohmic contacts. Ni/Au exhibited a lower contact resistance (~10^{-4} Ω cm^2 or lower) than Pd/Au (~10^{-3} Ω cm^2 or lower). Schottky barrier heights and ideality factors of Cr/Au and Ti/Au contacts were extracted by fitting current-voltage measurements to a back-to-back Schottky diode model. The ohmic behavior for Ni/Au and Pd/Au and the calculated Schottky barrier heights (0.39 and 0.50 eV for Cr/Au and Ti/Au, respectively) on SnS nanoribbons agree well with behavior predicted by Schottky–Mott theory and suggest a lack of Fermi level pinning.

Author Index

Bold page numbers indicate presenter

Author Index