2D Materials
Room A216 - Session 2D+EM+MI+NS-MoM

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties I

Moderator: Jeehwan Kim, Massachusetts Institute of Technology

8:20am **2D+EM+MI+NS-MoM-1 Extreme Fatigue Life of Graphene***, **Teng Cui**, S Mukherjee, P Sudeep, G Colas, J Tam,* University of Toronto, Canada*; P Ajayan,* Rice University*; C Singh, Y Sun, T Filleter,* University of Toronto, Canada

Materials can fail when subjected to cyclic loading at stress levels much lower than the ultimate tensile strength or yielding limit, which is known as mechanical fatigue. Understanding the fatigue behavior is critical for any emerging material in order to evaluate its long-term dynamic reliability. Two-dimensional (2D) materials have been widely applied to mechanical and electronic applications, where they are commonly subjected to cyclic stress. However, the fatigue life and underlying damage mechanisms of these atomically thin, nearly defect-free, materials are unknown. Here we show the first fatigue study of freestanding 2D materials, in particular graphene and graphene oxide (GO). Monolayer and few layer graphene and GO were found to all exhibit ultrahigh fatigue life of more than one billion cycles at large stress level in the GPa range. Such a remarkable fatigue life is higher than that of any material reported to date at similar stress levels. Graphene exhibits global and catastrophic fatigue failure preceded by bond reconfiguration near the defective site due to inhomogeneous charge distribution and higher potential energy. Graphene can fracture under cyclic loading but without progressive damage, which is distinct from the fatigue failure mechanism of any other materials. The presence of functional groups on GO imparts a local and progressive fatigue damage mechanism, which fits the macroscopic fatigue convention. The extraordinary fatigue life was found to diminish significantly when the material is scaled up in thickness (10s of layers). This work not only provides new fundamental insights into the widely observed fatigue enhancement behavior of graphene-embedded nanocomposites, but also serves as a starting point for the mechanical dynamic reliability evaluation of other 2D materials.

8:40am **2D+EM+MI+NS-MoM-2 Epitaxial Growth and Thermal Degradation of Monolayer MoS_2 on $SrTiO_3$ Single Crystal Substrates***, **Peiyu Chen**, W Xu, Y Gao, P Holdway, J Warner, M Castell,* University of Oxford, UK

Monolayer MoS_2 crystals grown on amorphous substrates such as SiO_2 are randomly oriented. However, when MoS_2 is grown on crystalline substrates, the crystal shapes and orientations are also influenced by their epitaxial interaction with the substrate. In the first part of this talk, we present the results from chemical vapor deposition growth of MoS_2 on three different terminations of single crystal strontium titanate ($SrTiO_3$) substrates: (111), (110), and (001). On all three terminations of $SrTiO_3$, the monolayer MoS_2 crystals try to align their <2 -1 -1 0>-type directions (i.e., the sulfur-terminated edge directions) with the <1 -1 0>-type directions on $SrTiO_3$. This arrangement allows near-perfect coincidence epitaxy between seven MoS_2 unit cells and four $SrTiO_3$ unit cells. On $SrTiO_3$(110), this even distorts the crystal shapes and introduces an additional strain detectable by photoluminescence (PL). Our observations can be explained if the interfacial van der Waals (vdW) bonding between MoS_2 monolayers and $SrTiO_3$ is greatest when maximum commensuration between the lattices is achieved. Therefore, a key finding of this study is that the vdW interaction between MoS_2 and $SrTiO_3$ substrates determines the supported crystal shapes and orientations by epitaxial relations.

Monolayer MoS_2 is also a wide-bandgap semiconductor suitable for use in high-temperature electronics. It is therefore important to understand its thermal stability. In the second part, we uncover the thermal degradation behavior of monolayer MoS_2 supported on $SrTiO_3$ in ultrahigh vacuum (UHV) because of sulfur loss. MoS_2 was found to degrade on the (111), (110), and (001) terminations of $SrTiO_3$ substrates in a similar way. The sulfur loss begins at 700 °C, at which point triangular etch trenches appear along the sulfur-terminated edge directions of the MoS_2 crystals (in scanning tunneling microscopy). The sulfur vacancies can be filled byannealing the crystals in a hot sulfur atmosphere, and the optical properties (by Raman spectroscopy and PL) of monolayer MoS_2 can nearly be fully recovered. At higher UHV annealing temperatures, the remaining Mo is oxidized by the $SrTiO_3$ substrates into MoO_2 and MoO_3. The initial sulfur loss and the formation of MoO_x are confirmed by X-ray photoelectron spectroscopy. The sulfur annealing no longer takes effect when all the Mo has been oxidized, which happens at a temperature between 800 °C and 900 °C in UHV. The MoS_2 crystal shapes are stable upon annealing until the residual MoO_3 particles evaporate at above 1000 °C. This infers that any triangular crystals that look intact under low-magnification optical microscopy and SEM may not mean pristine MoS_2.

9:00am **2D+EM+MI+NS-MoM-3 3D Printed and Injection Molded Polymer Matrix Composites with 2D Layered Materials***, **Sangram Mazumder**,* University of North Texas*; J Catalan,* University of Texas at El Paso*; N Hnatchuk, I Chen,* University of North Texas*; P Perez,* University of Texas at El Paso*; W Brostow, A Kaul,* University of North Texas

The two-dimensional layered materials (2DLMs), MoS_2 and WS_2, as well as three-dimensional (3D) graphite were infused in thermoplastic polymer matrices, specifically acrylonitrile butadiene styrene (ABS) and polyethylene terephthalate glycol (PETG). Two techniques were explored for the production of these composites into dog-bone structures for mechanical testing, which included 3D printing and injection molding. The ductility of the composites was generally seen to decrease with the addition of the fillers compared to the otherwise ductile polymer matrix counterparts. Also, changes in Young’s modulus, yield and tensile strengths, as well as percent strain at fracture, were analyzed as a function of filler loadings. The effect of processing technique on microstructures was also investigated by scanning electron microscopy of the fracture surfaces which revealed the presence of microstructural defects in the form of voids in the injection molded samples, which act as stress concentrators in the composite samples. Additionally, dynamic friction data of the composites was measured in an attempt to exploit the traditional, inherent solid phase lubricating properties of the 2DLMs. Graphite was indeed seen to lower dynamic friction in case of 3D printed PETG and injection molded ABS. Also, MoS_2 and WS_2 were found to reduce friction in 3D printed PETG and ABS. Graphite being an intrinsically good conductor, while the other 2DLMs explored, specifically MoS_2 and WS_2 given their semiconducting nature, can also be used as avenues for introducing electrical conductivity within these otherwise insulating parent polymer matrices. Thermal conductivity was also found to increase in both ABS and PETG composites containing graphite, MoS_2 and WS_2, irrespective of their processing routes. The use of 2DLM-based polymer composites remains an area that is bound to open up avenues for a wide range of applications in the future related to wearable electronics and sensors with low-cost additive manufacturing approaches.

9:20am **2D+EM+MI+NS-MoM-4 Semiconducting WS_2 and h-BN Inks for Printing Optically-active Nanodevices***, **Jay A. Desai**,* University of Texas at El Paso*; S Mazumder, A Kaul,* University of North Texas

We present our work on dispersions of WS_2 and h-BN using cyclohexanone and terpineol (C/T) as the solvent to subsequently print prototype nanodevices. Current-voltage measurements, Raman spectroscopy, and photoluminescence spectroscopy were used to characterize the properties of these inks produced by various sonication techniques such as horn tip sonication, magnetic stirring and shear mixing. Both photodetector and capacitive heterostructure devices were formed with these materials. From this analysis, the photoresponsivity and detectivity of the graphene-WS_2-graphene heterostructure devices were calculated to be ~ 0.86 A/W and ~ 10^{13} J, respectively. Capacitance-voltage (*C-V*) and *C*-frequency (*f*) measurements were also conducted, where the *V* was swept from – 6 V to + 6 V, while the change in *C* was measured from *f* ~ 20 kHz up to 3 MHz to gain insights into the nature of the graphene-WS_2 interface. An all-inkjet-printed graphene-h-BN-graphene capacitors were fabricated and leakage current density, $J_{Leakage}$, of up to ~ 0.072 μA/mm^2 and *capacitance density* of up to ~ 2.4 μF/cm^2 is reported. Finally, the influence of temperature, frequency, and LED illumination on the performance of the graphene-h-BN-based capacitor is explored with the help of *capacitance density*-voltage measurements at different parameters to promote the all-inkjet-printed capacitor for photosensitive detector applications.

9:40am **2D+EM+MI+NS-MoM-5 Transparent PEDOT:PSS Based Electro-Chromic/Thermal Devices With Excellent Durability For Applications In Smart Electronics***, **Hossein Sojoudi**, S Nemani,* University of Toledo

Thin-film electro-thermal/chromic devices were fabricated by utilizing PEDOT:PSS as the active conductive electrode thin-film and a compliant flexible polyurethane/ glass substrate as the building block. PEDOT:PSS exhibits electrochromic properties by undergoing an electrochemical redox reaction when an external stimulus in the form of electric potential is induced across the film. One major advantage of this technology is that it requires significantly lesser power per unit area and the color switching can be bi-stable in either transparent (oxidation) or dark blue (reduction) states. This low powered, controlled tuning in transparency of PEDOT:PSS was achieved by coupling doped PEDOT:PSS films with graphene as counter electrode, sandwiched between a solid-state electrolytic medium while maintaining high level of transparencies ~85% at peak oxidation levels. A high color contrast and improved coloration efficiency of 75% coupled with low power densities of 0.96 W/m^2, envisions its used in smart windows and visors. The mechanical self-assembly approach of graphene can be regulated by controlling the wavelength of wrinkles generated by inducing measured pre-strain conditions and regulating the modulus contrast of the materials used, which control the level of transparency, conductivity, and hydrophobic nature of the electrode(s). The transparency of wrinkled few layered graphene with an induced biaxial pre-strain = 0.36 was found to be 95% at 550 nm. We have also harnessed the electrothermal nature of PEDOT:PSS to achieve significant thermal responses at the expense of low power inputs to achieve temperatures as high as ~100°C due to joule heating in the doped PEDOT:PSS thin films. The absorbance and transmittance spectra for PEDOT:PSS were studied using a UV-VIS spectrometer at various oxidation and reduction states by applying biased voltage in the range of 2-5 Volts in varying cycles to determine electrochromic/thermal reversibility under induced strains, and electrothermal nature at various additive concentrations. These exceptional properties of the polymer, coupled with high work-function graphene electrodes can be envisioned to develop in-tandem smart electronic windows with tunable transmittances and heating responses for applications in automobile, aerospace, and service industries.

10:00am **2D+EM+MI+NS-MoM-6 Edge Dominated Graphene/h-BN Lateral Hybrid Nanostructures for Electronic and Spintronic Applications*, Gour P. Das*,** IIT Kharagpur India, India

For hybrid 2D nanostructures, the prime challenge is to control the electronic structure of edges that play a dominant role in tuning their structural, electronic, magnetic and other properties. Such heterostructures have been fabricated in-plane as well as perpendicular to the 2D plane, the latter constituting a class known as van der Waals heterosturctures. We have studied, using first principles approach, the electronic structure as well as transport properties of graphene/h-BN lateral hetero-nanoribbons of finite width, in order to probe the role of edge atoms and edge geometry on the resulting device behavior. For example, edge B doped zigzag graphene nanoribbons (ZGNRs) leads to spin filter based device [1]. We have investigated the origin of the spin filtering property in edge B-doped zigzag graphene nanoribbons (ZGNRs) and provide a guide to preparing a graphene based next-generation spin filter based device. While 100% edge B doping in ZGNR results in semiconductor to metal transition, 50% edge B doping shows half-metallicity when doped edge is unpassivated. Zero-bias transmission function of the other configurations shows asymmetric behavior for the up and down spin channels, thereby indicating their possible application potential in nano-spintronics.

In another related study [2], we have systematically varied the number of C-C or B-N units present in the graphene/*h*-BN hetero nanoribbon (G/BNNR), and have investigated their electronic as well as magnetic properties. Systems with both N or B terminated edges, undergo a semiconductor-to-semimetal-to-metal transition with the increase in the number of C-C units for a fixed ribbon width. The spin density distribution indicates significant localization of the magnetic moments at the edge carbon atoms, that gets manifested when the number of C-C units is greater than 2 for most of the structures.

** Work done in collaboration with Soubhik Chakrabarty, Tisita Das, Ranjit Thapa and Yoshiyuki Kawazoe.*

References :

[1] “Origin of spin polarization in an edge boron doped zigzag grapheme nanoribbon: a potential spin filter”, Soubhik Chakrabarty, A H M Abdul Wasey, Ranjit Thapa and G. P. Das, Nanotechnology **29**, 345203 (2018).

[2] “Tuning the electronic and magnetic properties of graphene/h-BN hetero nanoribbon: A first-principles investigation”, Tisita Das, Soubhik Chakrabarty, Y. Kawazoe and G. P. Das, AIP Advances **8**, 65111 (2018)

10:40am **2D+EM+MI+NS-MoM-8 Engineering Interfaces in the Atomically-Thin Limit*, Deep Jariwala,*** University of Pennsylvania **INVITED**

The isolation of a growing number of two-dimensional (2D) materials has inspired worldwide efforts to integrate distinct 2D materials into van der Waals (vdW) heterostructures. While a tremendous amount of research activity has occurred in assembling disparate 2D materials into “all-2D” van der Waals heterostructures, this concept is not limited to 2D materials alone. Given that any passivated, dangling bond-free surface will interact with another via vdW forces, the vdW heterostructure concept can be extended to include the integration of 2D materials with non-2D materials that adhere primarily through noncovalent interactions. I will present our work on emerging mixed-dimensional (2D + nD, where n is 0, 1 or 3) heterostructure devices. Two distinct examples of gate-tunable p-n heterojunctions with anti-ambipolar field efect will be presented. The anti-ambipolar field effect observed in the above systems is also shown generalized to other semiconducting heterojunction systems and extended over large areas with practical applications in wireless communication circuits. Recent work on high performance 2D/3D triodes will also be presented.

The second part of talk will focus on engineering interfaces on photovoltaic devices from 2D semiconductors such as transition metal dichalcogenides (TMDCs).High efficiency inorganic photovoltaic materials (e.g., Si, GaAs and GaInP) can achieve maximum above-bandgap absorption as well as carrier-selective charge collection at the cell operating point. Experimental demonstration of light confinement in ultrathin (< 15 nm) Van der Waals semiconductors (MoS$_2$, WS$_2$ and WSe$_2$) leading to nearly perfect absorption will be demonstrated concurrently with record high quantum efficiencies. Ongoing work on addressing the key remaining challenges for application of 2D materials and their heterostructures in high efficiency photovoltaics which entails engineering of interfaces and open-circuit voltage will be presented in addition to on going work on probing of buried metal/semiconductor interfaces with sub 50 nm resolutions as well as near field luminescence spectroscopy. I will conclude by giving a broad perspective of future work on 2D materials from fundamental science to applications.

11:20am **2D+EM+MI+NS-MoM-10 Ultrasoft Slip-mediated Bending in Few-layer Graphene*, Jaehyung Yu,*** *E Han, E Annevelink, J Son, E Ertekin, P Huang, A van der Zande,* University of Illinois at Urbana-Champaign

A challenge and opportunity in nanotechnology is to understand and take advantage of the breakdown in continuum mechanics scaling laws as systems and devices approach atomic length scales. Such challenges are particularly evident in two-dimensional (2D) materials, which represent the ultimate limit of mechanical atomic membranes as well as molecular electronics. For example, after more than a decade of study, there is no consensus on the bending modulus of few layer graphene, with measured and predicted values ranging over two orders of magnitude, and with different scaling laws. However, comparing these studies is challenging because they probe very different and often fixed curvatures or magnitudes of deformation. To unravel the discrepancy, a systematic measurement of bending stiffness versus deformation is needed. The results have practical implications on predicting and designing the stiffness of many 2D mechanical systems like origami/kirigami nanomachines, stretchable electronics from 2D heterostructures, and resonant nanoelectromechanical systems.

In this study, we combine atomistic simulation and atomic scale imaging to theoretically and experimentally examine the bending behavior of few-layer graphene. First, we experimentally probe the nanoscale bending by laminating few-layer graphene over atomically sharp steps in boron nitride and imaging the cross-sectional profile using aberration-corrected STEM. Second, we use DFT simulations to examine the bending of few-layer graphene under compression. By measuring the nanoscale curvatures, we extract the simulated and experimental bending modulus while varying both the number of layers and the degree of nanoscale curvature.

We find remarkable agreement between the theory and experiment and observe an unexpected curvature dependent bending stiffness of few-layer graphene that deviates from continuum scale bending mechanisms. We find that the bending stiffness of few layer graphene versus curvature corresponds with a gradual change in scaling power with thickness from cubic to linear. We find that the transition in scaling behavior originates from a transition from shear, slip and the onset in superlubricity between the graphene layers at the van der Waals interface, verified by a simple Frenkel-Kontorova model. Our results provide a unified model for the bending of 2D materials and show that their multilayers can be orders of magnitude softer than previously thought, among the most flexible electronic materials currently known.

11:40am **2D+EM+MI+NS-MoM-11 Experimental Study on Vanadium Oxides Films by Sputtering***, **Chuan Li,*** National Yang Ming University, Taiwan, Republic of China*; J Hsieh,* Ming Chi University of Technology, Taiwan, Republic of China*; C Su,* National Yang Ming University, Taiwan, Republic of China

Vanadium is noteworthy for its multivalence states of the four adjacent oxidation states 2–5. The oxides of vanadium(II-V) presents various colors in aqueous solution as $[V(H_2O)_6]^{2+}$ (lilac), $[V(H_2O)_6]^{3+}$ (green), $[VO(H_2O)_5]^{2+}$ (blue) and $[VO(H_2O)_5]^{3+}$ (yellow). Because of the broad range of oxidation states, vanadium oxides can be both an amphoteric oxide and an oxidizing/reducing agent. Thus vanadium oxides are used as precursors and catalysts as well in many industrial processes.

By its nature of multivalence, vanadium oxides have been widely used in devices for memory, photonics, and optoelectronics. Through articulately harnessing on phase transitions between metal and compound, vanadium oxides can be produced with specific properties for targeted functions. For example, one of the stoichiometric oxides, VO_2, vanadium dioxide is thermochromic which a phase change occurs at a temperature above 68°C from the semiconducting monoclinic microstructure to the almost conductive tetragonal structure. Correspondingly the high optical transmittance in the range of near-infrared also switches to high reflectance.

In this study, we fabricate vanadium oxide thin films by sputtering using vanadium targets by adjusting the oxygen flow rate to have amorphous vanadium oxides. The temperature during deposition is room temperature. To monitor the chamber condition, optical emission spectrometer is employed to record the optical spectra change following different oxygen flow rates fed into the chamber. To have a crystalline phase of as-deposited films, a rapid thermal annealing process is set up and the time and temperature of annealing shall be investigated to determine the appropriate operational range.

Atomic Scale Processing Focus Topic

Room A214 - Session AP+2D+EM+PS+TF-MoM

Area Selective Deposition and Selective-Area Patterning

Moderators: Satoshi Hamaguchi, Osaka University, Japan, Eric A. Joseph, IBM Research Division, T.J. Watson Research Center

8:40am **AP+2D+EM+PS+TF-MoM-2 Surface Pre-functionalization of SiN_x and SiO_2 to Enhance Selectivity in Plasma–Assisted Atomic Layer Etching***, **Ryan Gasvoda,*** Colorado School of Mines*; Z Zhang, S Wang, E Hudson,* Lam Research Corporation*; S Agarwal,* Colorado School of Mines

To manufacture semiconductor devices in the current sub-7-nm node, stringent processing windows are placed on all aspects in manufacturing including plasma-etching. In recent years, atomic layer etching (ALE) has emerged as a patterning technique that can provide high etch fidelity, directionality, layer–by–layer removal, and selectivity to meet the tight processing windows. Plasma–assisted ALE of SiO_2 and SiN_x is of particular interest since Si-based dielectrics are commonly used throughout the entire fabrication process. Typically, these materials are etched in a cyclic ALE process consisting of two sequential half–cycles: fluorocarbon (CF_x) deposition from a fluorocarbon plasma followed by an Ar plasma activation step. Etch selectivity can be achieved through careful manipulation of the plasma and processing parameters. To further increase overall etch selectivity, we have proposed a methodology that selectively pre–functionalizes the SiO_2 or SiN_x surface with hydrocarbons prior to ALE. Recently, we showed that an etch blocking graphitic hydrofluorocarbon film will readily accumulate on a pre–functionalized SiO_2 surface.

In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and *in situ* 4–wavelength ellipsometry to monitor the surface reactions, film composition, and net film thickness during the entire ALE process. We show that aldehydes can be used to functionalize SiN_x with extremely high selectivity to SiO_2 surfaces. During ALE on bare SiN_x, a thick graphitic fluorocarbon film accumulates on the surface and can stop all etching after cycle 5. This is attributed to inefficient removal of both the C and N from the surface. To enhance removal and prevent graphitic carbon accumulation, we graft a branched hydrocarbon aldehyde to the SiN_x surface. This branched hydrocarbon provides an abundance of $–CH_3$ groups which allows for greater C and N removal possibly via HCN formation, thus lowering overall graphitic carbon formation. This retardation of the graphitic hydrofluorocarbon film formation leads to both an overall increase in the etch per cycle and the number of ALE cycles that can be run before an etch stop is observed.

9:00am **AP+2D+EM+PS+TF-MoM-3 Area-selective Atmospheric-pressure Spatial ALD of SiO_2 using Interleaved Back-etch steps Yielding Selectivity > 10 nm***, A Mameli,* Holst Centre / TNO, The Netherlands*; F Roozeboom, **Paul Poodt,*** Holst Centre / TNO, The Netherlands, Netherlands

Area-selective atomic layer deposition (AS-ALD) has great potential in reducing cost by maskless device manufacturing of patterned layers. Still, in this new *bottom-up* approach the selectivities currently obtained for film growth on patterned growth areas vs. that on the non-growth areas are often very limited. Also the substrate throughput values for conventional low-pressure ALD is too low for industrial acceptance.(1,2) In this work we present a process for AS-ALD of SiO_2 using intermittent plasma etch-back steps to increase the selectivity above 10 nm film thickness.(3) In addition, the deposition process itself is performed in a spatial ALD reactor at atmospheric pressure which allows for achieving high throughput.(4)

AS-ALD of SiO_2 on a substrate with pre-patterned SiO_2 and ZnO areas was demonstrated using a highly chemo-selective inhibitor that chemisorbs preferentially on the non-growth area (ZnO) while allowing the deposition of SiO_2 on the growth area (SiO_2). In order to maximize the process selectivity, a blanket fluorocarbon plasma etch-back step was interleaved after every 110 ALD cycles. This way, selective SiO_2 deposition up to ~ 30 nm film thickness was demonstrated. Furthermore, X-ray Photoelectron Spectroscopy was carried out to verify the selectivity of the process: no Si was detected (detection limit 0.3 at. %) on the non-growth area, demonstrating the high selectivity of the process.

The process presented here combines selective inhibitor chemisorption, plasma-based spatial ALD with high deposition rates and plasma etch-back steps to correct for selectivity loss. This approach is compatible with *roll-to-roll* and *sheet-to-sheet* concepts and can therefore enable high-throughput AS-ALD on large-area and flexible substrates.

[1] A. Mameli, *et al.*, *ACS Nano*, **11**, 9303 (2017).

[2] F.S.M. Hashemi, *et al.*, *ACS Nano*, **9**, 8710 (2015).

[3] R. Vallat, *et al.*, *J. Vac Sc. Technol. A*, **35**, 01B104 (2017).

[4] P. Poodt, *et al.*, *Adv. Mater.*, **22**, 3564 (2010).

9:20am **AP+2D+EM+PS+TF-MoM-4 Mechanisms of Precursor Blocking during Area-selective Atomic Layer Deposition using Inhibitors in ABC-type Cycles***, M Merkx,* Eindhoven University of Technology, The Netherlands*; D Hausmann,* Lam Research Corporation*; E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; T Sandoval,* Universidad Técnica Federico Santa María, Chile*; **Adrie Mackus**[1],* Eindhoven University of Technology, The Netherlands, Nederland

The development of new processes for area-selective atomic layer deposition (ALD) is currently motivated by the need for self-aligned fabrication schemes in semiconductor processing. For example, area-selective ALD processes for dielectric-on-dielectric deposition are being considered for fully self-aligned via (FSAV) fabrication schemes in advanced interconnect technology.

Instead of solely relying on surface functionalization prior to ALD, an novel strategy to area-selective ALD involves the dosing of inhibitor molecules during every cycle in an ABC-type recipe.[1,2] By using small molecules that can be dosed in vapor-phase as inhibitor, this approach is compatible with industrial process flows. Moreover, the reapplication of the inhibitor molecules during every cycle allows for the use of a plasma as the co-reactant, which broadens the range of materials that can be deposited selectively. In contrast to conventional approaches to area-selective ALD based on self-assembled monolayers (SAMs), very little is known about how small inhibitor molecules can block the ALD growth.

In this contribution, insight into the mechanisms of precursor blocking by inhibitor molecules as obtained from in-situ Fourier transform infrared spectroscopy (FTIR) and density functional theory (DFT) calculations will be discussed. Area-selective ALD of SiO_2 using acetylacetone (Hacac) as inhibitor will be described as a model system, illustrating various mechanisms that can contribute to the loss of selectivity. It was found that at saturation, Hacac adsorbs through a mixture of chelate and monodentate bonding configurations. Hacac in monodentate configuration is displaced from the surface when exposed to bis(diethylamino)silane precursor molecules, which limits the selectivity. Strategies for improving

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[1] **Paul Holloway Award Winner**

the selectivity based on the understanding from these studies will be discussed.

[1] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels, and A.J.M. Mackus, ACS Nano **11**, 9303 (2017).

[2] A.J.M. Mackus, M.J.M. Merkx, and W.M.M. Kessels, Chem. Mater. **31**, 2 (2019).

9:40am **AP+2D+EM+PS+TF-MoM-5 Area-Selective Deposition of TiO_2 using Isothermal Integrated Atomic Layer Deposition and Atomic Layer Etching in a Single Reaction Chamber***, **Gregory Parsons**, S Song, H Saare,* North Carolina State University **INVITED**

Several new approaches are emerging where chemical etching is being coupled with atomic layer deposition to achieve area-selective deposition of dielectrics and metals. During ALD, selectivity is generally lost when undesired nuclei form on the targeted non-growth surface. These undesired nuclei can sometimes be removed by periodic etching, improving the overall selectivity. However, it is not known to what extent these coupled deposition/etching sequences can proceed while maintaining good selectivity. As desirable deposition and etching reactions proceed, other changes in the process can occur to enhance unwanted nucleation and/or impede desired etching, thereby limiting the net selectivity. Recent experiments in our lab have used in-situ probes to explore coupled thermal ALD and ALE super-cycles, performed sequentially under isothermal conditions in a single reaction chamber, to achieve area selective deposition of TiO_2 on SiO_2 with hydrogen-terminated silicon (100) as the desired non-growth surface. We find that as ALD/ALE super-cycles proceed, small changes occur in the ALD and ALE reactions, particularly during the transition from ALD to ALE, or from ALE to ALD. Also, modeling studies allow us to quantitatively analyze the ASD results and compare our findings to other known approaches. These insights will be helpful to understand opportunities and challenges in advanced atomic scale reactions and process implementation.

10:40am **AP+2D+EM+PS+TF-MoM-8 Area-Selective Atomic Layer Deposition of Metal Oxides on an Inhibitor-Functionalized SiO_2 Surface***, **Wanxing Xu**,* Colorado School of Mines*; P Lemaire, K Sharma, D Hausmann,* Lam Research Corporation*; S Agarwal,* Colorado School of Mines

The continued downscaling of modern semiconductor devices together with the incorporation of 3D architectures places new constrains on conventional lithography techniques. To enable further advances in patterning process, new techniques will be required for next-generation devices to overcome the challenges of limiting the growth of desired materials in a specific area. One method to address these issues is area-selective atomic layer deposition (ALD), which provides the opportunity to build defined patterns from the bottom-up at the atomic-level accuracy. In this study, we will focus on area-selective ALD of metal oxides including ZrO_2 and Al_2O_3 with a metal as the growth surface and inhibitor-functionalized SiO_2 as the non-growth surface. To inhibit ALD, the SiO_2 surfaces were functionalized with aminosilane inhibitors through the vapor phase or with a solution-based method. The functionalized SiO_2 surfaces were characterized by transmission Fourier transform infrared (FTIR) spectroscopy, ellipsometry, and water contact angle measurements. Metal oxides including ZrO_2 and Al_2O_3 were deposited by ALD using metal precursors and H_2O over a temperature range of 150-250 °C. *In situ* attenuated total reflection FTIR spectroscopy was utilized to identify the surface reactions sites and absorbed surface species during ALD. In addition, the corresponding film growth was measured using *in situ* four-wavelength ellipsometry.

Using *in situ* optical diagnostics, we show the mechanism for the breakdown in selectivity during area-selective ALD on a SiO_2 surface that is functionalized with aminosilanes. The infrared spectra show that aminosilane inhibitors react with almost all of the surface –SiOH groups forming Si–O–Si–R bonds on the surface (see Figure 1). After repeated exposure of the functionalized SiO_2 surface to TEMAZ and ZTB, these precursors react with Si–O–Si bonds without surface –SiOH groups (see Figure 2). Although small growth in the first few ALD cycles is not detected by *in situ* ellipsometry, growth inhibition breaks down after an increased number of ALD cycles. These results suggest that it is an additional requirement to suppress other reactions with a higher activation energy barrier during ALD expect removing main surface reactive sites through surface functionalization. To further impede growth of metal oxides on functionalized SiO_2 surface, a two-step functionalization method was developed to passivate the SiO_2 surface while providing additional steric blocking for the underlying substrates. Comparative studies were carried out to evaluate the effect of different functionalization methods on suppressing the nucleation during ALD.

11:00am **AP+2D+EM+PS+TF-MoM-9 Area-selective Deposition Achieved in a Continuous Process using Competitive Adsorption***, **Taewon Suh**, Y Yang, K Lao, R DiStasio, Jr., J Engstrom,* Cornell University

A significant challenge for single-nm fabrication technologies is the development of area selective deposition (ASD) processes, particularly for device structures with exposed metallic and dielectric surfaces on patterned, often three dimensional, substrates. A number of techniques have been proposed and examined for ASD processes, particularly with respect to ALD, and these include the use of "permanent" blocking layers in the form of SAMs, and repetitive deposition/etch cycles. Some success has been reported with these techniques, but they possess potential drawbacks. An ideal ASD process should be fast, preferably vapor phase, and leave no residue on the non-growth surface. One technique that can possibly provide this is the use of competitive adsorption to induce area selective deposition, where a co-adsorbate is chosen that will bind much more strongly to one surface vs. another. A significant challenge concerning this approach is avoiding direct reactions between the co-adsorbate and the thin film precursor in the case of ALD, and also the co-reactant in the case of CVD. We are coupling quantum mechanical calculations of co-adsorbate/thin-film precursor/substrate interactions with experiments using our coupled micro-reactor/UHV surface analysis system. We have examined the effect of a class of unsaturated hydrocarbons as co-adsorbates on the CVD growth of ZrO_2 thin films using a Zr amido-coordination complex as the thin film precursor and O_2 as the co-reactant. The substrates were SiO_2 and Cu, and we examined the effects of both temperature, T_s = 120-240 °C, and the partial pressure of the co-adsorbate hydrocarbon. DFT calculations predict that the binding energies of these hydrocarbons are at least a factor of two larger on Cu vs. those on SiO_2. For CVD growth of ZrO_2 thin films as thick as 22 nm (growth rates of ~ 1 $nm\text{-}s^{-1}$), we find that the co-introduction of the hydrocarbon results in linear growth with time on a SiO_2 substrate, with no apparent incubation time, while essentially no growth is observed on Cu. *In situ*, post-deposition analysis with XPS reveals ZrO_2 thin films on SiO_2, and only adventitious carbon and less than a monolayer of Zr on the Cu surface. Consistent with a model based on competitive adsorption, we find that selectivity is eventually lost at sufficiently high substrate temperatures or sufficiently low partial pressures of the hydrocarbon co-adsorbate. Finally, we will report on the CVD growth on patterned Cu/SiO_2 substrates where we observe deposition only on those areas covered by SiO_2. We will conclude with a discussion of the promise and challenges of this approach for ASD concerning both ALD and CVD processes.

11:20am **AP+2D+EM+PS+TF-MoM-10 Surface Chemistry during Plasma-Assisted ALE: What Can We Learn from ALD?***, **Sumit Agarwal**,* Colorado School of Mines **INVITED**

Due to ever decreasing device dimensions and the introduction of 3D device architectures, it is challenging to operate within a narrow processing window using conventional plasma etching. One method to address the demands of the next-generation of devices is atomic layer etching (ALE) which provides high fidelity, selectivity, and directionality, and layer-by-layer removal. Plasma-assisted ALE has been extensively studied for a variety of materials, including Al_2O_3, HfO_2, Si, and Si–based dielectrics. Plasma-assisted ALE of SiO_2 or SiN_x typically uses two sequential steps in a cyclic fashion: CF_x deposition from a C_4F_8/Ar plasma followed by an Ar plasma activation step. However, the surface chemistry during plasma ALE is not well understood. In this study, we used *in situ* attenuated total reflection Fourier transform infrared (ATR–FTIR) spectroscopy and *in situ* four-wavelength ellipsometry during ALE to monitor the surface reactions, film composition, as well as the net film thickness. Similar to area-selective atomic layer deposition, we show that surface functionalization prior to ALE can be used to alter the etch per cycle. Using this methodology, I will discuss how selective functionalization of SiO_2 or SiN_x can be used to alter the selectivity during plasma-assisted ALE.

Materials and Processes for Quantum Information, Computing and Science Focus Topic
Room B231-232 - Session QS+EM+MN+NS-MoM

High Coherence Qubits for Quantum Computing

Moderators: Vivekananda Adiga, IBM, T.J. Watson Research Center, Martina Esposito, Oxford University, UK

8:20am **QS+EM+MN+NS-MoM-1 Measurement of a Two-Level-System Dipole Distribution in a Nanoscale Aluminum Oxide Barrier***, **Chih-Chiao Hung**, N Foroozani, K Osborn,* University of Maryland

Random atomic-sized material defects, identified as two-level systems (TLS), have garnered wide interest because they cause decoherence in superconducting qubits. TLSs often arise in the nonlinear element, the Josephson junction, which is typically made of amorphous aluminum oxide. This material is a clear concern in qubits due to a substantial loss tangent in bulk: large area JJs. However, detail on the dipole moments of individual TLSs is generally lacking but is fundamental to defect-qubit coupling. We have recently developed a method to study individual dipole moments in thin dielectric films with a quantum regime resonator using an electrical bridge of capacitors. We have now extended this technique to a different material, aluminum oxide, using a smaller nanoscale thicknesses and barrier volume. The geometry of the device allows extraction of the individual dipole moments within the central layer of a superconductor-aluminum oxide-superconductor trilayer. This new study also produced a greater statistical sample of TLS dipoles than previous work. Preliminary analysis allows us to extract a dipole moment distribution with a clear mean value. This information on aluminum oxide can be used in the future modeling of qubits and the future characterization of qubit materials.

8:40am **QS+EM+MN+NS-MoM-2 Mapping Quantum Systems to Quantum Computers using Symmetry***, **Daniel Gunlycke**, S Fischer, S Hellberg, S Policastro, S Tafur,* U.S. Naval Research Laboratory

Quantum entanglement is a natural phenomenon in quantum mechanics that has enormous significance in quantum information science, including quantum computing. It enters quantum states in quantum algorithms through the application of multi-qubit quantum logic operations such as the CNOT and Ising gates. While deliberate entanglement adds power and efficiency to algorithms, unintentional entanglement can be undesirable for a variety of reasons. Unintentional entanglement adds complexity, making the outcome of a given algorithm more difficult to understand, as well as more sensitive to errors. Furthermore, it can be an indication that an algorithm has not been optimized. If we could transfer entanglement from our algorithms into the bases that define our systems, then we could potentially reduce our algorithms, including the qubit requirement. Such algorithm reductions will be of outmost importance for resource-limited, noisy intermediate-scale quantum (NISQ) computers.

In this presentation, we will demonstrate how such a reduction could be achieved for the simulation of quantum systems using symmetry. In addition to reducing the needed resources, our quantum computer calculations show a significant improvement in accuracy.

9:00am **QS+EM+MN+NS-MoM-3 History of Superconducting Qubit Coherence and the Current Challenges***, **Hanhee Paik**,* IBM T.J. Watson Research Center **INVITED**

Since the first demonstration of a few nanoseconds of coherent oscillations in 1999, a tremendous amount of effort has been put in to improve coherence of superconducting qubits. A modern day superconducting qubits show typically 100 microseconds of coherence times which allowed us to demonstrate a few simple quantum computing applications that led rapid growth of quantum computing industry. To build a full fault-tolerant universal quantum computing system, however, we still need a couple more orders of magnitude improvement in the superconducting qubit coherence, the solution to which, we believe, is in the qubit materials. In this talk, I will review the history of the superconducting qubit coherence research and what we learned about the materials for quantum computing at milli-kelvin temperatures, and I will discuss the current challenges of the coherence studies in the conjunction with the challenges in material science research.

9:40am **QS+EM+MN+NS-MoM-5 Loss and Decoherence Benchmarking of Superconducting Transmon Qubits***, **Jonas Bylander**,* Chalmers University of Technology, Sweden **INVITED**

We are engineering a superconducting quantum processor within the Wallenberg Center for Quantum Technology [1] in Sweden and the project OpenSuperQ [2] of the European Union's Flagship on Quantum Technology. Here we will present our engineering approach for high-coherence superconducting quantum hardware. We have studied the temporal stability of relaxation and dephasing in transmon qubits [3]. Our qubits are made of aluminum on silicon; they have reached average T_1 relaxation times of about 70 us. The T_2^* decoherence time, as measured in a Ramsey fringe, is practically relaxation-limited. By collecting statistics during measurements spanning several days, we reveal large fluctuations of qubit lifetimes – the standard deviation of T_1 is about 15 us – and find that the cause of fluctuations is parasitic, near-resonant two-level-systems (TLS). Our statistical analysis shows consistency with an interacting-TLS model. Interacting TLS also cause low-frequency capacitance fluctuations, ultimately leading to frequency noise and dephasing of the qubit state. These discoveries are important for creating stable superconducting circuits suitable for high-fidelity quantum gates in quantum computing applications.

[1] www.wacqt.se

[2] www.opensuperq.eu

[3] J. J. Burnett, A. Bengtsson, M. Scigliuzzo, D. Niepce, M. Kudra, P. Delsing, and J. Bylander, "Decoherence benchmarking of superconducting qubits" arXiv:1901.04417

10:40am **QS+EM+MN+NS-MoM-8 Towards PAMBE Grown Nitride Superconductors for Epitaxial Josephson Junctions and Quantum Circuits***, **Christopher Richardson**, A Alexander, C Weddle,* Laboratory for Physical Sciences*; M Olszta, B Arey,* Pacific Northwest National Laboratory **INVITED**

Low microwave loss superconducting circuit components are a necessity of fabricating high-fidelity superconducting qubits. Accordingly, significant research has focused on making high-quality planar resonators from elemental and nitride superconductors. Josephson junctions are the nonlinear component of superconducting qubits, that also need to be high performance. Interestingly, superconducting qubits all use Josephson junctions fabricated from aluminum and aluminum oxide using the double angle evaporation process. Details of this alternative design will be presented.

Plasma assisted Molecular beam epitaxy (PAMBE) is used to grow niobium titanium nitride alloys ($Nb_xTi_{1-x}N$) and wide bandgap nitride (AlN) superconductors directly on sapphire wafers. This combination of nitride materials provides sufficient degrees of freedom that synthesis of an epitaxial Josephson junction may be possible. Using a structure first approach to design optimization, the structural, surface topology, chemical characteristics, and superconducting critical temperature of these films are used for optimization of the growth conditions before resonators are fabricated and tested.

Growth results of NbTiN and AlN films, bi-layer insulator-superconductor structures and trilayer superconductor-insulator-superconductor structures will be presented along with superconducting properties.

11:20am **QS+EM+MN+NS-MoM-10 Josephson Junction Metrology for Superconducting Quantum Device Design***, **Ruichen Zhao**, M Bal, J Long, R Lake, X Wu, C Rae McRae, H Ku, H Wang, D Pappas,* National Institute of Standards and Technology (NIST)

Josephson junctions (JJs) are the power horses that drive the development of superconducting quantum technologies in the past decades. The non-linear inductance of JJs turns superconducting circuitry into a high-coherence two-level system that forms the foundation for quantum information processing [1]. They also enable Josephson parametric amplification that significantly improves the measurement of the fragile quantum state of superconducting qubits, mechanical oscillators or spins [2]. Consequently, the characterization of junction inductance becomes essential for the design and fabrication of these superconducting quantum devices.

Here, we present a systematic approach to characterize the micron-size JJs made from a new process. This new recipe extends from our previous work on nanoscale overlapping qubit junctions [1]. First, we collect statistics of the normal-state resistance over 2000 JJs through the room-temperature automated probing test. Second, we use Ambegaokar-baratoff formula to map the normal-state junction resistance into Josephson inductance [3]. Then we extract and investigate the process bias of our JJs. Based on this new information of JJs variation, we proposed a new JJ process which could potentially provide better control over the Junction inductance and therefore, deliver more reliable parameters for the device design.

[1] X. Wu, et al. "Overlap junctions for high coherence superconducting qubits." Applied Physics Letters 111.3: 032602 (2017).

[2] M. Malnou, et al. Optimal operation of a Josephson parametric amplifier for vacuum squeezing. Physical Review Applied, 9(4), 044023 (2018).

[3] V. Ambegaokar, & A. Baratoff, "Tunneling between superconductors." Physical Review Letters, 10(11), 486 (1963).

11:40am **QS+EM+MN+NS-MoM-11 Superconducting Metamaterial Resonator Spectrum and Interaction with Qubit***, **Haozhi Wang**, S Indrajeet, M Hutchings, M LaHaye, B Plourde,* Syracuse University*; B Taketani, F Wilhelm,* Saarland University

Metamaterial transmission line resonators fabricated from superconducting thin films can be designed to exhibit novel mode spectra like a high density of modes in the same frequency range where superconducting qubits are typically operated. We demonstrate the mode spectrum of a metamaterial resonator made of single layer of Nb and the coupling quality factor of the modes. We also present a series of low-temperature measurements of such a superconducting metamaterial resonator coupled to a flux-tunable transmon qubit. We observe Rabi vacuum crossing when performing transmission measurement of the metamaterial resonator as we tune the qubit frequency through many of the metamaterial resonances and we are able to track the qubit using a separate conventional resonator to read out the qubit state.

Thin Films Division
Room A122-123 - Session TF+EM+MI+MN+OX+PS-MoM

Functional Thin Films: Ferroelectric, Multiferroics, and Magnetic Materials

Moderators: Christophe Vallee, LTM - MINATEC - CEA/LETI, France, Jessica Kachian, Intel Corporation

8:20am **TF+EM+MI+MN+OX+PS-MoM-1 A Room-Temperature Magnetoelectric Multiferroic made by Thin Film Alchemy***, D Schlom, **Megan Holtz**,* Cornell University **INVITED**

Materials that couple strong ferroelectric and ferromagnetic order hold tremendous promise for next-generation memory devices. Meticulous engineering has produced novel ferroelectric and multiferroic materials, although known single-phase multiferroics remain limited by antiferromagnetic or weak ferromagnetic alignments, by a lack of coupling between the order parameters, or by having properties that emerge only well below room temperature. Here we construct single-phase multiferroic materials in which ferroelectricity and strong magnetic ordering are coupled near room temperature. Starting with hexagonal LuFeO_3—a geometric ferroelectric with planar rumpling—we introduce individual monolayers of ferrimagnetic LuFe_2O_4 within the LuFeO_3 matrix, that is, $(\text{LuFeO}_3)_m/(\text{LuFe}_2\text{O}_4)_1$ superlattices. The rumpling of the LuFeO_3 drives the ferrimagnetic LuFe_2O_4 into a ferroelectric state, reducing the LuFe_2O_4 spin frustration. This increases the magnetic transition temperature to 281K for m=9. Moreover, the ferroelectric order couples to the ferrimagnetism, enabling direct electric-field control of magnetism at 200 kelvin. Further, charged ferroelectric domain walls align at LuFe_2O_4 layers, resulting in charge transfer which increases the magnetic moment. We are currently pursuing higher temperature multiferroics by incorporating cubic spinels with high magnetic ordering temperatures, such as CoFe_2O_4, into the LuFeO_3 matrix. Our results demonstrate a design methodology for creating higher-temperature magnetoelectric multiferroics through epitaxial engineering.

9:00am **TF+EM+MI+MN+OX+PS-MoM-3 Magnetic Losses in FeGa/NiFe/Al_2O_3 Laminates for Strain-Mediated Multiferroic Micro-Antenna Applications***, **Kevin Fitzell**, A Acosta, C Rementer, D Schneider, Z Yao,* University of California, Los Angeles*; C Dong,* Northeastern University*; M Jamer, D Gopman, J Borchers, B Kirby,* National Institute of Standards and Technology (NIST)*; N Sun,* Northeastern University*; Y Wang, G Carman, J Chang,* University of California, Los Angeles

The ability to reduce the size of antennae would enable a revolution in wearable and implantable electronic devices. Multiferroic antennae, composed of individual ferromagnetic and piezoelectric phases, could reduce antenna size by up to five orders of magnitude through the efficient coupling of magnetization and electric polarization via strain. This strategy requires a material with strong magnetoelastic coupling and acceptable magnetic losses at high frequency.

Galfenol ($\text{Fe}_{84}\text{Ga}_{16}$ or FeGa) is a promising candidate material due to its large magnetostriction (200 με), large piezomagnetic coefficient (5 ppm/Oe), and high stiffness (60 GPa), but it is highly lossy in the GHz regime. On the other hand, Permalloy ($\text{Ni}_{81}\text{Fe}_{19}$ or NiFe) is a soft magnetic material that has very low loss in the GHz regime, with a ferromagnetic resonance (FMR) linewidth of 10 Oe, but almost no magnetostriction. In this work, nanoscale laminates containing alternating layers of FeGa and NiFe were fabricated via DC magnetron sputtering to combine the complementary properties of the two magnetic phases, resulting in a composite material with a small coercive field, narrow FMR linewidth, and high permeability (Rementer et al., 2017). Optical magnetostriction measurements confirmed that these laminates retain the large saturation magnetostriction of FeGa (200 με) while enhancing the piezomagnetic coefficient (7 ppm/Oe), allowing for optimal piezomagnetic actuation at substantially reduced magnetic bias fields. Furthermore, multiferroic composites incorporating these magnetic laminates were studied via polarized neutron reflectometry, demonstrating uniform rotation of the individual layers' magnetization with an applied electric field across distances much larger than the exchange length of either material.

Due to the metallic nature of these FeGa/NiFe multilayer composites, however, resulting devices would be inefficient due to the generation of eddy currents at high frequency. To mitigate these losses, ultrathin layers of Al_2O_3 were incorporated into the multilayer materials to reduce the conductivity and mitigate the generation of eddy currents. The effect of Al_2O_3 thickness, FeGa:NiFe volume ratio, and multilayer architecture on the soft magnetic properties was also studied, resulting in a 50% reduction in the FMR linewidth. Optimized magnetic laminates were shown to exhibit a small coercive field (<20 Oe), narrow ferromagnetic resonance linewidth (<50 Oe), and high relative permeability (>500) while maintaining excellent magnetoelastic coupling, showing great promise for the use of FeGa/NiFe/Al_2O_3 laminates in strain-mediated micro-scale communications systems.

9:20am **TF+EM+MI+MN+OX+PS-MoM-4 Multiferroic Gd-substituted HfO_2Thin Films***, **John Hayden**, F Scurti, J Schwartz, J Maria,* Pennsylvania State University

Modern ferroelectric technologies utilize perovskite structured materials, which have limited Si compatibility and modest bandgaps requiring thick films to reduce leakage current, hindering their implementation in realizable thin film devices. HfO_2 has been extensively researched as a gate dielectric thin film with excellent Si processing compatibility and has recently been found to exhibit ferroelectricity induced by a combination of impurity substitution, mechanical confinement by capping, intergranular surface area, and film thickness effects. This work investigates the microstructural characteristics, the ferroelectric response, and the potential for concomitant magnetic properties in sputtered Gd:HfO_2 thin films.

Gd-substituted HfO_2 thin films are a promising candidate as a multiferroic material, due to the presence of the magnetically active Gd^{3+} ion. Though substituting with Gd is known to induce ferroelectricity in HfO_2, the magnetic properties of Gd:HfO_2 have yet to be studied in depth. In this study, Gd:HfO_2 films are fabricated on TaN substrates by radio frequency sputtering of a composite Gd metal and HfO_2 oxide target in a mixed Ar and O_2 atmosphere. Grazing incidence x-ray diffraction is used to evaluate the suppression of the paraelectric monoclinic phase and stabilization of the ferroelectric orthorhombic phase. Electrical polarization measurements are used to study the room temperature spontaneous polarization in TaN/Gd:HfO_2/TaN metal-insulator-metal capacitors. Surface morphology of the films is characterized using atomic force microscopy, while magnetic properties are measured by variable temperature magnetometry. Initial magnetometry shows that Gd-substituted HfO_2 exhibits remnant magnetization at room temperature.

The scalability and simplicity of Gd:HfO_2, if it exhibits magnetoelectric coupling, make it an attractive model system for future developments in thin film multiferroics, having potential impacts for spintronics and other magnetoelectronic devices.

9:40am **TF+EM+MI+MN+OX+PS-MoM-5 Epitaxial Growth of Antiferromagnetic NiO Films by Off-axis Sputtering for Spintronic Devices***, A Churikova, G Beach,* Massachusetts Institute of Technology*; **Larry Scipioni**, A Shepard, J Greer, T Newhouse-Illige,* PVD Products, Inc.

High-quality epitaxial growth of antiferromagnetic thin films is essential for future spintronic devices, as it allows small antiferromagnetic domain sizes and efficient electrical manipulation of domain walls via reading and writing currents. Antiferromagnetic materials are candidates for ultrafast operation due to THz antiferromagnetic spin dynamics, high packing densities due to the absence of stray magnetic fields, and stability due to insensitivity to external magnetic fields [1,2]. Meanwhile, the long spin diffusion lengths [3] and theoretically predicted superfluid transport of spin currents [4] in antiferromagnetic insulators are crucial for low-power device operation. The electrical control of magnetic spin textures has been thus far realized in epitaxially grown NiO on MgO substrates [5] and ferrimagnetic maghemite (γ−Fe2O3) and magnetite (Fe3O4) thin films [6].

We report the preparation of antiferromagnetic NiO thin films with (111) orientation on *c*-plane sapphire (1000) substrates by off-axis RF magnetron sputtering from a NiO target. The off-axis angle was 45°, and the sputtering pressure was 5 mTorr. Samples were grown with thicknesses ranging from 5 – 50 nm, and with growth temperatures from room temperature to 600°C, to determine optimum conditions. Structural characterization by x-ray diffraction demonstrates a high degree of epitaxy across a range of deposition temperatures and thicknesses. The deposition temperature and thickness dependence of epitaxial quality is investigated, with a characterization of the strain state, mosaicity, and crystallographic relationship between substrate and film. Evidence for antiferromagnetic order forming domains in NiO is provided via magnetic characterization of the films. Our results are essential for the optimization of the fabrication of high quality epitaxial antiferromagnetic films for practical spintronics devices.

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[2] V. Baltz, A. Manchon, M. Tsoi, T. Moriyama, T. Ono, and Y. Tserkovnyak, Rev. Mod. Phys. 90, 015005 (2018).

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10:00am **TF+EM+MI+MN+OX+PS-MoM-6 Structural and Magnetic Properties of CoPd Alloys for Non-Volatile Memory Applications***, S Gupta, J Abugri, B Clark,* University of Alabama*; P Komninou,* Aristotle University of Thessaloniki*; **Sujan Budhathoki**, A Hauser, P Visscher,* University of Alabama

A study of perpendicular magnetic anisotropy (PMA) CoPd alloys is presented as a simple means of pinning MgO-based perpendicular magnetic tunnel junctions (pMTJs) for spin transfer torque magnetic tunnel junction (STT-MRAM) applications. A compositional study of the Co_xPd_{100-x} alloys at 50 nm thickness showed that the maximum coercivity and anisotropy was found for $Co_{25}Pd_{75}$. Perpendicular magnetic tunnel junction stacks were deposited using different compositions of CoPd. Current-in-plane tunneling measurements indicated that the TMR values roughly correlated with the coercivity and anisotropy of the single layers. A thickness study indicated that the alloy was fully perpendicular for thicknesses as low as 20 nm. Various seed layers were employed to optimize the coercivity of the $Co_{25}Pd_{75}$ layer. Magnetometry, X-ray diffraction (XRD), scanning electron microscopy (SEM) and high resolution transmission electron microscopy studies were carried out to relate the magnetic and structural properties of these layers. These studies showed that the highest coercivity $Co_{25}Pd_{75}$ was achieved on a seed layer of Ta/Pd which helped to crystallize the CoPd layer in an fcc (111) orientation.

10:40am **TF+EM+MI+MN+OX+PS-MoM-8 Size Effects of the Electromechanical Response in Ferroic Thin Films: Phase Transitions to the Rescue***, **Nazanin Bassiri-Gharb**,* Georgia Institute of Technology **INVITED**

Silicon-integrated ferroelectric thin films have been leveraged over the last two decades for fabrication of high performance piezoelectric microelectromechanical systems (MEMS) devices. Ceramic $Pb(Zr_xTi_{1-x})O_3$(PZT) thin films have been often the material of choice, due to their large electromechanical response, especially at morphotropic phase boundary compositions (MPB at x ~0.52), where co-existence of multiple crystallographic distortions can enhance extrinsic electromechanical contributions. However, ferroelectric thin films suffer from extrinsic size effects that lead to deteriorated piezoelectric properties in thin and ultra-thin films. Here we report on different strategies for processing of thin films with enhanced piezoelectric response with respect to traditionally processed PZT thin films. Specifically, we will discuss preparation of superlattice-like polycrystalline PZT thin films through chemical solution depositions, polycrystalline relaxor-ferroelectric thin films (PMN-PT), and finally alternative non-ferroelectric compositions, where the electric field-induced phase transitions can result in substantial enhancement in thinner films, even where traditional

11:20am **TF+EM+MI+MN+OX+PS-MoM-10 Ferroelectrics Meet Ionics in the Land of van der Waals***, S Neumayer,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; J Brehm,* Vanderbilt University*; M McGuire,* Oak Ridge National Laboratory*; M Susner,* Air Force Research Laboratory*; E Eliseev,* National Academy of Sciences of Ukraine*; S Jesse, S Kalinin,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory*; A Morozovska,* National Academy of Sciences of Ukraine*; S Pantelides,* Vanderbilt University*; N Balke, **Petro Maksymovych**,* Center for Nanophase Materials Sciences, Oak Ridge National Laboratory

Van der Waals crystals of metal thiophosphates can be thought of as derivatives of transition metal dichalcogenides where 1/3 of metal atoms is replaced with diphosphorous, thereby stabilizing the remaining 2/3 of metal ions in low oxidation states.1 Consequently, thiophosphates enable ultrathin magnetic, ferroelectric and Mott insulating materials, in q2D materials while also providing new opportunities for multifunctional interfaces .

Of particular interest is $CuInP_2S_6$, where ferroelectricity emerges out of ionically conducting state .2,3 In this work, we discuss unusual and perhaps anomalous properties observed in $CuInP_2S_6$ in both states.

$CuInP_2S_6$ exhibits giant negative electrostriction ($Q_{33} = -3.2\ m^4/C^2$), which leads to large piezoelectric coefficients despite small polarization values and increase of Tc with applied pressure. It's the only material other than polymer PVDF for which such behavior is experimentally confirmed. Density functional theory reveals that the reason for negative electrostriction is a slight movement of Cu ions into the van der Waals gap due to anharmonicity of the potential well.4 Moreover, under high compressive strain, Cu starts to form interlayer bonds with sulfur across the van der Waals gap, leading to an additional phase of high polarization. Consequently, the potential distribution exhibits 4 instead of the usual two minima - a quadruple well, that is precisely tunable by strain. In the paraelectric state above ~70°C, Cu ion mobility drastically increases. Intriguingly, Cu can be reversibly extracted out of the lattice without visible damage. Finally, the selenide sibling $CuInP_2Se_6$, exhibits a lower transition temperature and propensity toward antiferroelectric ordering under the effect of depolarizing fields. In this material, we have for the first time observed piezoelectric response confined to domain walls (opposite to ferroelectrics), fulfilling the long-standing predictions for polar antiferroelectric domain walls and providing a new model system for emergent properties of topological defects in ferroic order parameter fields.

Research sponsored by Division of Materials Science and Engineering, Basic Energy Sciences, US Department of Energy. Microscopy was conducted at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

1Susner et al, Adv. Mater. 29,1602852 (2018)

2Neumayer et al, Phys. Rev. Materials **3**, 024401 (2019)

3Balke et al, ACS Appl. Mater. Interfaces 10, 27188 (2018)

[4]Brehm et al, in review

11:40am **TF+EM+MI+MN+OX+PS-MoM-11 Adsorption-controlled Epitaxial Growth of the Hyperferroelectric Candidate LiZnSb on GaSb (111)***, D Du, P Strohbeen,* University of Wisconsin - Madison*; H Paik,* Cornell University*; C Zhang, P Voyles, **Jason Kawasaki**,* University of Wisconsin - Madison

A major challenge for ferroelectric devices is the depolarizing field, which competes with and often destroys long-range polar order in the limit of ultrathin films. Recent theoretical predictions suggest a new class of materials, termed hyperferroelectics [1], should be immune to the depolarizing field and enable ferroelectric devices down to the monolayer limit. Here we demonstrate the epitaxial growth of hexagonal LiZnSb, one of the hyperferroelectric candidate materials, on GaSb (111) substrates. Due to the high volatility of all three atomic species, we find that stoichiometric films can be grown in a thermodynamically adsorption-controlled window, using an excess zinc flux. Outstanding challenges remain in controlling the point defects of LiZnSb and in controlling polytypism. While the films primarily grow in a hexagonal “stuffed wurtzite” phase (space group $P6_3mc$), which is has the desired polar structure, there exists a competing cubic “stuffed zincblende” polymorph that is nonpolar (*F-43m*). We will discuss our strategy towards controlling defects and polytypism in LiZnSb, which is based in large part on the wurtzite – zincblende polytypism observed in InAs. We will also present preliminary electrical measurements on phase pure ferroelectric capacitor structures.

This work was supported by the Army Research office (W911NF-17-1-0254) and the National Science Foundation (DMR-1752797).

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2D Materials
Room A226 - Session 2D+AP+EM+MI+MN+NS+PS+TF-MoA

Nanostructures including Heterostructures and Patterning of 2D Materials

Moderator: Deep Jariwala, University of Pennsylvania

1:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-1 Tailoring and Patterning 2D Material Interfaces Through Chemical Functionalization*, Arend van der Zande,*** University of Illinois at Urbana-Champaign **INVITED**

Two-dimensional materials are all surface, so any change in the surface chemistry affects the entire material. This offers a challenge and an opportunity to engineering the material properties and new device behavior. There are many strategies to altering the chemical structure of 2D materials, yet one of the most successful is the chemical functionalization with low energy plasmas such as hydrogen and fluorine. Functionalization enables phase changes within materials to dramatically alter their properties, can be applied post synthesis and device fabrication, and is compatible with lithography for spatial patterning. Most studies of chemical functionalization focus on single functionalization of single 2D materials, yet there are many opportunities when applying the principles of chemical functionalization to spatially engineer the properties though in plane interfaces or out of plane in heterostructures.

First, we will examine selective etching with XeF_2 to pattern heterostructures using graphene etch stops. These techniques are self-limiting, yet scalable, and enable the patterning of 2D heterostructures into 3D multilayer circuitry. Moreover, devices like encapsulated graphene transistors fabricated with these techniques have exceptionally low contact resistances and mobilities which approach theoretical limits.

Second we will present a new strategy for tailoring the stoichiometry of functionalized graphene compounds through the systematic control of the ratio between adatoms. We demonstrate new ternary HFG compounds and reversible switching of material stoichiometry via the sequential exposure of graphene to low energy H plasma and XeF_2 gas. By patterning regions of different functionalization on a single chip, we perform direct comparisons and show spatially controlled tuning of the relative surface properties such as wettability, friction, electronic conductivity and molecular adhesion. Taken together, these studies show that chemical functionalization offers new atomically precise nanofabrication and materials engineering techniques for scalable engineering of circuitry along all three dimensions.

2:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-3 Dual-Route Hydrogenation of the Graphene/Ni Interface*, Rosanna Larciprete,*** CNR-Institute for Complex Systems, Roma, Italy*; D Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy*; M Trioni,* CNR-Institute of Molecular Science and Technologies, Milano, Italy*; P Lacovig, L Bignardi, S Lizzit,* Elettra - Sincrotrone Trieste, Trieste, Italy*; R Martinazzo,* Università degli Studi di Milano, Milano, Italy

Although the high surface-to-weight ratio would make graphene (Gr) one of the most promising material for hydrogen accumulation, up to now only moderate gravimetric density values of 1-2% have been obtained at room temperature (RT). The ultimate H coverage is limited by the competition between the adsorption and desorption/abstraction processes and by the elastic energy that accumulates in the C lattice once puckered by the local sp3rehybridization of the C atoms binding hydrogen. Moreover, for epitaxial Gr on metals, the substrate-induced Gr corrugation might modulates periodically H adsorption. In this respect, the Gr/Ni(111) interface appears much more favorable than other graphene/metal systems, as the limitations due to the presence of the moirè supercell vanish due to commensurate relation between the Gr and Ni(111) lattices. Moreover, hydrogenation might be favored by the peculiar reactivity of Gr/Ni(111).This issues motivated a re-investigation of the interaction of this particular interface with hydrogen.

In this study [1]we used x-ray photoelectron spectroscopy (XPS) and near edge x-ray absorption fine structure spectroscopy (NEXAFS) to follow the RT hydrogenation of Gr/Ni(111) and determined the configuration of the hydrogenated interface by scanning tunneling microscopy (STM). We found that hydrogenation proceeds through a dual path that includes hydrogen chemisorption on top of the graphene followed by a slow but continuous intercalation below graphene. At low coverage H atoms predominantly adsorb as monomers and chemisorption saturates when ≈ 25% of the surface is hydrogenated. The formation of C−H bonds determines new components in the C 1s core level spectrum that are attributed by DFT calculations to C atoms directly bonded to H and to their first neighbors. In parallel with chemisorption, with a much lower rate, H atoms intercalate below Gr and bind to Ni surface sites. Thermal programmed desorption measurements showed that chemisorbed hydrogen is released around 600 K, whereas the intercalated phase desorbs abruptly slightly below 400 K. Then the Gr cover, besides offering a storage volume for the intercalated H, stabilizes it above room temperature rising by a few tens of kelvins the H2 release temperature with respect to the bare Ni(111) surface.

The effectiveness of these results can be expanded by using Ni substrates with large specific surface, as nanoparticles or nanostructured foils, which, when covered with Gr, might become media where hydrogen can be loaded and stored above room temperature.

[1] D. Lizzit et al. ACS Nano 13 (2019) 1828

2:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-4 Assembly of Arrays of Predefined Monolayer Features into vdW Heterostructure by a Continuous Exfoliate-align-Release Process*, Vu Nguyen,*** *H Taylor,* University of California at Berkeley

One of the major challenges of van der Waals (vdW) integration of 2D materials is the high-yield and -throughput assembly of pre-defined sequence of monolayers into heterostructure arrays. Although a variety of techniques have been developed to exfoliate the 2D materials from the source and deterministically place them onto a target substrate, they typically can transfer only either a wafer-scale blanket or a small flake at a time with uncontrolled size and shape. Here we present a method to exfoliate arrays of lithographically defined monolayer MoS_2 and WS_2 features from multilayer sources and directly transfer them in a deterministic manner onto target substrates. The continuous exfoliate-align-release process, without the need of an intermediate carrier substrate, was enabled by a new transfer medium fabricated by spin-coating a low-crosslinked and transparent adhesive on a transparent, electrostatically active backing material with low surface energy. MoS_2/WS_2 vdW heterostructure arrays produced by this method were characterized, showing coupled photoluminescence between the monolayers. Light-emitting devices using WS_2 monolayer were also demonstrated, proving the functionality of the fabricated materials. This method promises to produce large-area monolayer and multiplex heterostructure arrays with capability to integrate with existing semiconductor manufacturing equipment.

3:00pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-5 van der Waals Heterojunction Photothermoelectric Effect in MoS_2/Graphene Monolayers*, Yunqiu Kelly Luo,*** The Ohio State University*; T Zhou,* University at Buffalo, State University of New York*; M Newburger,* The Ohio State Univesity*; R Bailey-Crandell, I Lyalin,* The Ohio State University*; M Neupane,* U.S. Army Research Laboratory*; A Matos-Abiague,* Wayne State University*; I Zutic,* University at Buffalo, State University of New York*; R Kawakami,* The Ohio State University

Two-dimensional (2D) van der Waals (vdW) heterostructures provide a vast playground for exploring new phenomena due to its unique ability to tailor and combine dissimilar materials with atomic precision. In particular, the combination of graphene and transition metal dichalcogenides (TMDC) garners immense interest due to their novel optoelectronic, valleytronic and spintronic properties. Here, we report the observation of a highly tunable vdW heterojunction photothermoelectric effect (HPTE) in dual-gated MoS_2/graphene heterostructures, identified by a signature six-fold photocurrent pattern as a function of heterojunction bias and carrier density. In stark contrast to photovoltaic and photothermionic effects, we discover a new mechanism arising from photoexcitation of hot electrons in graphene and subsequent thermoelectric transport across the vdW junction. While analogous to lateral photothermoelectric effects at quasi-1D junctions in single layers, the vertical geometry of HPTE offers area scaling of 2D active regions and establishes, for the first time, the photothermoelectric response in vdW heterostructures. Operating at both low (18 K) and room temperatures, the discovery of HPTE creates new possibilities for electrically-tunable broadband photodetectors and atomically-thin spin caloritronic devices.

3:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-6 Formation of Edge-bonded MoS_2-graphene Nanoribbons by On-surface Synthesis*, Mark Haastrup,*** *M Mammen, J Rodríguez-Fernández, J Lauritsen,* Aarhus University, Denmark

2D materials exhibiting unique material properties have the potential for a huge impact on our future. Graphene, as the first discovered truly 2D material, has been extensively studied. However, the lack of an intrinsic band gap makes it inadequate for electronic and optical devices. MoS_2 from the family of transition metal dichalcogenides has been intensively investigated for its possibility to be used in future applications. The vision is to integrate various 2D materials to realise an actual device. However, the actual assembly of these materials with high controllability remains a challenge. Vertical heterostructures, supported by Van der Waals interactions, have already been realised by manually stacking 2D materials on top of each other[1]. An ultimate thin device can be realised by creating lateral heterostructures with atomically sharp interfaces where each material is directly bonded to another. Currently, methods for in-plane bonding of MoS_2 to other materials (e.g. graphene) are limited due to poor structural match. One possible solution is to develop selective bottom-up methods for synthesis of molecular nanostructures by self-assembly.

This study aim to investigate the fundamental nature of bonding of graphene nanoribbons (GNRs) to the edges of MoS_2 nanoparticles by scanning tunnelling microscopy (STM). The aim is to synthesise GNRs from precursor molecules through a thermally activated Ullmann reaction already used elsewhere[2,3]. After initial growth of MoS_2, it is necessary to anneal in a hydrogen atmosphere to activate the edges to facilitate the attachment of an intermediate structure of poly(para-phenylene) (PPP) wires. STM reveals the PPP wires have an affinity for the corners of the MoS_2 nanoparticles with a distance, obtained from line scans across the adsorption site, consistent with a covalent C-S bond.

[1]: Pant et al., Nanoscale, 2016, 8, 7, 3870-3887

[2]: Cai et al., Nature, 2010, 466, 7305, 470–473

[3]: Basagni et al., J. Am. Chem. Soc., 2015, 137, 5, 1802-1808

4:00pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-8 The Effects of Metal-modification and Two Dimensional (2D) Lamellar Structure on Catalytic Performance of MFI Zeolite for Ethylene Conversion into Liquid Aromatics*, Laleh Emdadi,*** *L Mahoney, D Tran, I Lee,* US Army Research Laboratory

The effects of two dimensional (2D) meso-/microporous structure and metal modification with gallium or zinc on catalytic performances of lamellar MFI zeolites in ethylene conversion reaction to liquid aromatics were investigated. Dual template technique was used to synthesize the 2D zeolite and metal modification of the zeolite was carried out by wet impregnation method. The results of multiple analysis techniques such as TEM, XRD, Ar adsorption-desorption, UV-Visible spectroscopy, and H_2-TPR showed that the zeolite structure is a pivotal factor for controlling the type of metal dopant species forming on zeolite, their size, and their distribution. Adding metal dopants to 2D zeolite structures improved the yield of liquid aromatics and selectivity for mono-benzene alkylated aromatics compared to their microporous commercial MFI analogies while decreased the coke formation rate. Zinc loaded lamellar MFI had the most efficient catalytic performance among all studied catalysts with lowest amount of total coke and highest fraction of light coke including mono-benzene alkylated aromatics determined by combination of different techniques such as FTIR, UV-Vis, MS-temperature programmed oxidation (TPO), FTIR-TPO, and GC-MS. This can be explained by higher accessibility of reactants to active sites and facilitated transport of products and coke precursors from lamellar structure of this zeolite and the lower Brønsted/Lewis acid site ratio of this catalyst provided by metal modification which is more suitable for ethylene aromatization and suppresses the formation of heavy coke species. The catalytic performance of zeolite catalyst can be tuned by modulating both the textural and acidity properties of the zeolite structure. The metal modified 2D lamellar MFI zeolites as bifunctional catalysts open an avenue for converting large reactant molecules to desired products by designing a catalyst with an optimal structure, acidity, and dispersion of metal dopants.

4:20pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-9 Structural Stability of Graphene Nanoflakes:From the View Point of Aromaticity**, *M Ushirozako, H Matsuyama, A Akaishi,* ***Jun Nakamura,*** The University of Electro-Communications (UEC-Tokyo), Japan

Recently, nano-scale graphene nanoflakes (GNFs) have attracted great attention as one of the promising materials for electronics and spintronics. Kim *et al*. have successfully fabricated GNFs with various sizes up to 35 nm and have reported that the photoluminescence property of GNFs depends on the size and the edge shape [1]. From the view point of the structural stability of GNFs, we have not yet acquired the systematic comprehension with regard to effects of shapes and sizes of GNFs on the stability. In the present study, we have examined how the stability of GNFs is dominated by the edge shape and the size of GNFs, using first-principles calculations within the density functional theory.

In order to evaluate the stability of GNFs, we calculated the edge formation energy. First, we consider GNFs with the six-fold symmetry (D_{6h}) and classify them into zigzag GNFs (ZZGNFs) and armchair GNFs (ACGNFs). ACGNFs have two subtypes, AC(1) and AC(2), depending on whether carbon atoms are just at the corner of the outermost envelope hexagon of GNFs. We define the edge purity as the ratio of the number of carbon atoms at the edge unambiguously regarded as the armchair to the total number of edge atoms. The purity of AC(1) is higher than that of AC(2). The chemical formulae associated with ZZ, AC(1), and AC(2) are $C_{6n^2}H_{6n}$, $C_{18n^2-18n+6}H_{12n-6}$, $C_{18n^2-30n+12}H_{12n-12}$, respectively. In addition, we also evaluate the structural stabilities of triangular and rhombus GNFs.

We calculated the edge formation energy of the GNFs having up to 1200 carbon atoms as a function of the number of edge carbon atoms [3]. The formation energy of ZZGNFs is higher than that of ACGNFs irrespective of the size of GNFs. This instability of ZZGNFs is attributed to the presence of the so-called edge state. Indeed, it has also been shown that the formation energy of the zigzag graphene nanoribbon is higher than that of the armchair one [4]. It is noted that AC(2) is slightly more stable than AC(1), whereas the purity of AC(2) is lower than that of AC(1). Such peculiar stabilization can be reasonably explained in terms of the aromaticity of GNFs. The Nucleus Independent Chemical Shifts (NICS) values, which is averaged for the six-membered rings in GNFs, for AC(2) are lower than those for AC(1). This means AC(2) is more aromatic than AC(1). We will discuss the quantitative relationship between the stability and the aromaticity of GNFS.

[1] S. Kim et al., ACS Nano, **6**, 9, 8203 (2012)

[2] W. Hu *et al*., J. Chem. Phys. **141**, 214704 (2014)

[3] A. Akaishi, M. Ushirozako, H.Matsuyama, andJ.Nakamura, Jpn.J.Appl.Phys. **57**, 0102BA(2018)

[4] S. Okada. Phys. Rev. B, **77**, 041408 (2008)

4:40pm **2D+AP+EM+MI+MN+NS+PS+TF-MoA-10 Wafer-scale 2D-3D Mixed Heterostructures Enabled by Remote Epitaxy through Graphene*, Jeehwan Kim,*** Massachusetts Institute of Technology **INVITED**

The current electronics industry has been completely dominated by Si-based devices due to its exceptionally low materials cost. However, demand for non-Si electronics is becoming substantially high because current/next generation electronics requires novel functionalities that can never be achieved by Si-based materials. Unfortunately, the extremely high cost of non-Si semiconductor materials prohibits the progress in this field. Recently our team has invented a new crystalline growth concept, termed as “remote epitaxy”, which can copy/paste crystalline information of the wafer remotely through graphene, thus generating single-crystalline films on graphene [1,2]. These single-crystalline films are easily released from the slippery graphene surface and the graphene-coated substrates can be infinitely reused to generate single-crystalline films. Thus, the remote epitaxy technique can cost-efficiently produce freestanding single-crystalline films including III-V, III-N, and complex oxides. This allows unprecedented functionality of flexible device functionality required for current ubiquitous electronics. I will also present detailed mechanism behind remote atomic interaction through graphene [2]. In addition, we have recently demonstrated a manufacturing method to manipulate wafer-scale 2D materials with atomic precision to form monolayer-by-monolayer stacks of wafer-scale 2D material heterostructures [3]. In this talk, I will discuss the implication of this new technology for revolutionary design of next generation electronic/photonic devices with combination of 3D/2D mixed heterostructures.

[1] Y. Kim, et al, and J. Kim, “Remote epitaxy through graphene enables two-dimensional material based layer transfer” ***Nature***, Vol. 544, 340 (2017)

[2] W. Kong, et al, and J. Kim, “Polarity govern atomic interaction through two-dimensional materials”, ***Nature Materials***, Vol. 17, 999 (2018)

[3] J. Shim, S. Bae, et al, and J. Kim, “Controlled crack propagation for atomic precision handling of wafer-scale two-dimensional materials” ***Science***, 362, 665 (2018)

2D Materials

Room A216 - Session 2D+AP+EM+MI+NS+PS+TF-MoA

2D Materials Growth and Fabrication

Moderator: Sarah Haigh, University of Manchester, UK

1:40pm **2D+AP+EM+MI+NS+PS+TF-MoA-1 Two-dimensional Non-layered Indium Sulfide for Electronic and Optical Applications***, **Jian Zhen Ou**, A Jannat, K Xu,* RMIT University, Australia

Tetragonal indium sulfide (In2S3) is a n-type semiconductor enabled by a unique ordered vacancy structure, which have interesting electronic and optical properties. However, its non-layered nature results in the challenge to realize its two-dimensional (2D) form. Here, we demonstrate two approaches to synthesize 2D In2S3. In the first approach, we grow 2D In2S3 with the thickness of single unit cell in wafer-scale using liquid metal as the reactant medium. The first principle calculation reveals that the 2D InsS3 has highly dispersive conduction band with low effective electron mass, forming multiple band-like electronic transport channels. The field effect mobility of the material is measured to be ~60 cm2 V−1 s−1 with a high degree of reproducibility. In the second approaches, we synthesize 2D In2S3 with the thickness of a few unit cells using the liquid phase exfoliation of the bulk powder. It is found that there is an ultra-thin layer of 2D hexagonal indium oxide (In2O3) formed during the exfoliation process, hence forming an inherent 2D In2O3/In2S3 heterostructure. The photoluminescent life time is enhanced compared to In2S3 alone and the NO2 gas sensing performance of the heterojunction is assessed under the illumination of visible light at room temperature. Excellent response and recovery kinetics are observed with the NO2 detection of limit of <0.5 ppb. These two representative examples demonstrate that 2D In2S3 can be a suitable candidate for high performance electronic and sensing devices.

2:00pm **2D+AP+EM+MI+NS+PS+TF-MoA-2 Synthesis of High Quality Monolayer Transition Metal Dichalcogenides using Direct Liquid Injection***, **Kathleen M. McCreary**, E Cobas, A Hanbicki, M Rosenberger, H Chuang, B Jonker,* U.S. Naval Research Laboratory

In recent years, interest in monolayer transition metal dichalcogenides (TMDs) has rapidly increased, spurred by the possibility for integration into a variety of technologies such as photodetection, flexible electronics, and chemical sensing. While fundamental investigations can be performed on exfoliated flakes or chemical vapor deposition synthesized isolated islands, the limited size resulting from these techniques poses a significant barrier forimplementation of TMDs in technological applications. To overcome these obstacles, new synthesis avenues should be explored. Here, we outline a novel technique that utilizes a commercially available Anneal Sys growth chamber equipped with direct liquid injection (DLI) heads for all precursors. The use of liquid, rather than solid precursors, provides fine control of both metal and chalcogen precursors leading to the synthesis of monolayer MoS_2 across cm^2 areas. Photoluminescence, Raman, XPS, and conductive AFM are used to evaluate DLI grown MoS_2, and indicate high quality material having low defect density, with metrics comparable to or better than exfoliated and chemical vapor deposition grown MoS_2.

2:20pm **2D+AP+EM+MI+NS+PS+TF-MoA-3 Understanding and Controlling the Growth of 2D Materials with Non-Equilibrium Methods and in situ Diagnostics***, **David Geohegan**, Y Lin, Y Yu,* Oak Ridge National Laboratory*; C Liu, G Duscher,* University of Tennessee Knoxville*; A Strasser,* University of Texas at Dallas*; A Puretzky,* Oak Ridge National Laboratory*; K Wang,* Intel Corporation, USA*; M Yoon, C Rouleau,* Oak Ridge National Laboratory*; S Canulescu,* DTU Nanolab, Technical University of Denmark*; P Rack,* University of Tennessee Knoxville*; L Liang, W Zhang, H Cai, Y Gu, G Eres, K Xiao,* Oak Ridge National Laboratory **INVITED**

Atomically-thin two-dimensional (2D) materials, including layered 2D transition metal dichalcogenide (TMD) semiconductors and their heterostructures, exhibit remarkable quantum properties that are envisioned for energy-efficient photovoltaics, flexible optoelectronics, catalysis, and quantum information science. However, significant synthesis and processing challenges currently limit the technologic development of these “all-surface” materials, including wafer-scale, bottom-up synthesis of uniform layers of crystalline 2D materials that are comparable in quality to exfoliated flakes of bulk materials. As-synthesized crystals of 2D TMDs display remarkable heterogeneity on both the atomistic level (e.g., vacancies, dopants, and edge terminations) and on the mesoscopic length scale (e.g., misoriented grains, layer orientations, and interactions with substrates and adsorbates) that can strongly influence the structure and electronic properties in 2D materials. This heterogeneity offers a serious challenge for synthesis and processing, yet offers a tremendous opportunity to tailor functionality.

Here we describe several approaches that are being developed for in situ diagnostic analysis and control of synthesis and heterogeneity. In addition to conventional vapor transport techniques, progress in laser-based approaches for 2D synthesis and modification, such as pulsed laser deposition (PLD) and pulsed laser conversion of precursors, are presented that permit control of the growth environment using time-resolved in situ diagnostics. The non-equilibrium advantages of PLD to form alloys and vertical heterojunctions are demonstrated using the tunable kinetic energy and digital nature of the process. Correlated atomic-resolution electron microscopy and atomistic theory are used to understand the size and stoichiometry of the “building blocks” deposited for synthesis and the forces that guide assembly. 2D crystals are grown directly on TEM grids within custom chambers and transmission electron microscopes where the ability to ‘see’ every atom in these atomically-thin crystals permits a unique opportunity to understand the forces governing their synthesis and functionality. In situ optical spectroscopy techniques are described to characterize the material’s evolving structure and properties, offering the opportunity to ‘close the loop’ between synthesis and optoelectronic functionality of 2D materials and heterostructures.

Research sponsored by the U.S. Dept. of Energy, Office of Science, Basic Energy Sciences, Materials Science and Engineering Div. (synthesis science) and Scientific User Facilities Div. (characterization science).

3:00pm **2D+AP+EM+MI+NS+PS+TF-MoA-5 Area-Selective Atomic Layer Deposition of 2D WS_2 Nanolayers***, **Shashank Balasubramanyam**[1],* Eindhoven University of Technology, The Netherlands, Noord Brabant*; M Merkx,* Eindhoven University of Technology, The Netherlands*; E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; A Mackus,* Eindhoven University of Technology, The Netherlands, Nederland*; A Bol,* Eindhoven University of Technology, The Netherlands, Netherlands

With continued downscaling of device dimensions, ultra-thin two dimensional (2D) semiconductors like WS_2 are considered as promising materials for future applications in nanoelectronics. At these nanoscale regimes, device fabrication with precise patterning of critical features is challenging using current top-down processing techniques. In this regard, area-selective atomic layer deposition (AS-ALD) has emerged as a promising candidate for bottom-up processing to address the complexities of nanopatterning. Till date, AS-ALD of metals[1] and dielectrics[2] have been successfully demonstrated. However, AS-ALD of 2D materials has remained elusive. In this contribution, we demonstrate area-selective deposition of 2D WS_2 nanolayers by using a three-step (ABC-type) plasma-enhanced ALD process.

AS-ALD of WS_2 was achieved by using acetylacetone (Hacac) inhibitor (A), bis(tertbutylimido)-bis(dimethylamido)-tungsten precursor (B), and H_2S plasma (C) pulses. This process resulted in immediate growth on SiO_2 while a significant nucleation delay was observed on Al_2O_3, as determined from *in-situ* spectroscopic ellipsometry (SE) and *ex-situ* X-ray photoelectron spectroscopy (XPS) measurements. The surface chemistry of this selective process was analysed by *in-situ* Fourier transform infrared spectroscopy (FTIR). The analyses revealed that the inhibitor adsorbed on the Al_2O_3 surface, blocking precursor adsorption, while little or no inhibitor adsorption was detected on the SiO_2 surface where WS_2 was readily deposited. Furthermore, the area-selective growth was demonstrated on SiO_2 samples with patterned Al_2O_3 on top. On SiO_2, WS_2 could be deposited with angstrom-level thickness control.

To improve the crystallinity, the AS-ALD WS_2 films were annealed at temperatures within the thermal budget of industrial semiconductor processing (≤ 450°C). The annealed films exhibited sharp Raman peaks, which is a fingerprint of highly crystalline WS_2. Furthermore, Raman line scans over the patterns showed very sharp peak intensity transitions at the

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[1] **TFD James Harper Award Finalist**

SiO_2-Al_2O_3 interface which confirmed that annealing had no impact on selectivity.

To summarize, this work pioneered the combination of two key avenues in atomic-scale processing: area-selective growth and ALD of 2D materials. It is expected that the results of this work will lay the foundation for area-selective ALD of other 2D materials.

[1] R. Chen and S.F. Bent, *Adv. Mater.* (2006).

[2] A. Mameli, M.J.M. Merkx, B. Karasulu, F. Roozeboom, W.M.M. Kessels and A.J.M. Mackus, *ACS Nano* (2017).

3:20pm **2D+AP+EM+MI+NS+PS+TF-MoA-6 Growth Behavior of Hexagonal Boron Nitride on Cu-Ni Binary Alloys***, **Karthik Sridhara,*** Texas A&M University*; J Wollmershauser,* U.S. Naval Research Laboratory*; L Nyakiti,* Texas A&M University*; B Feigelson,* U.S. Naval Research Laboratory

Controlled growth of large area n-layered chemical vapor deposited (CVD) hexagonal boron nitride (h-BN) is of great interest as a tunnel dielectric, and substrate for graphene and transition metal dichalcogenides (TMDs). The CVD growth of h-BN has been demonstrated on various transition metal catalytic substrates such as Cu, Ni, Pt and Fe. Of these metal substrates, Cu and Ni are frequently used due to their relative abundance and low cost. However, h-BN growth on Cu leads to monolayer films, and growth on Ni yields thicker, substrate grain-dependent films. Therefore, a cost-effective transition metal substrate is needed that will facilitate controlled n-layered h-BN growth.

In this work, we prepare isomorphous Cu-Ni binary alloys from 10-90 wt.% Ni by creating Ni-rich (Ni-Cu) and Cu-rich (Cu-Ni) alloys using electroplating of Cu on Ni foils and Ni on Cu foils, respectively. The electroplated foils are then annealed at ~1030° C for >5 hours to create Ni-Cu and Cu-Ni alloys. The alloys are subsequently polished mechanically to create a planarized surface suitable for h-BN growth. The surface morphology before and after polishing is assessed using a scanning electron microscope (SEM). Energy dispersive spectroscopy (EDS) characterization of the alloys confirms a designed stoichiometry at every weight percent. h-BN is grown on the alloys using atmospheric pressure chemical vapor deposition (APCVD) at 1030° C, with ammonia borane as the precursor, and H_2/N_2 as the carrier gas flowing at ~200 sccm. Cu and Ni foils are used as control samples for this study. Fourier transform infrared reflection absorption spectroscopy (FT-IRRAS) is used to confirm and characterize h-BN growth directly on Cu, Ni and alloy substrates. SEM is performed to evaluate the h-BN film and crystal morphology. The results indicate that the h-BN growth behavior on Ni-Cu is different than on Cu-Ni alloys. A trend of decreasing h-BN amount with reducing Ni concentration is observed on Ni-Cu alloys while no such trend is observed on Cu-Ni alloys. Additionally, there are large (~20 µm) multilayer and monolayer single crystals of h-BN on Ni-Cu alloys, and predominantly monolayer crystals and films of h-BN on Cu-Ni alloys. The difference in growth behavior is studied using x-ray photoelectron spectroscopy (XPS) and electron backscattering diffraction (EBSD), which reveal that the alloy surface composition determines the h-BN growth. This work demonstrates how Cu-Ni alloy substrate of different compositions, along with CVD growth conditions, can be used to control h-BN growth.

4:00pm **2D+AP+EM+MI+NS+PS+TF-MoA-8 Chemical Deposition of Vanadium Disulfide on Silicon for Optoelectronic Applications***, **Mathias Fraccaroli,*** R Gassilloud, S Cadot,* CEA-LETI, France*; B Pelissier,* LTM, Univ. Grenoble Alpes, CNRS, France*; C Vallée,* LTM, Univ. Grenoble Alpes, CEA-LETI, France*; A Sylvestre,* G2Elab, Univ. Grenoble Alpes, France

In recent years, the search for alternative substrates to standard semiconductors (Si, Ge, SiGe, III-V, II-VI, etc.) has intensified. In this context, the transition metal dichalcogenides (TMDs) have recently emerged as candidates for the realization of original devices in a context of diversification of functionality (more than Moore). Indeed, these lamellar materials, structurally similar to graphene, have a great diversity of electrical behaviors, from the semiconductor to the metal, as well as many interesting properties (piezoelectricity and photoluminescence for MoS_2 and WS_2, even ferromagnetism by the addition of a dopant, temperature resistive transition for TaS_2, ...). The interest of the scientific community for this family of materials is growing, mainly for the most famous of them: MoS_2 and WS_2. Among this family, vanadium disulfide (VS_2)remains little studied and the development of a transferable synthesis method to an industrial scale remains a real challenge.

In this context, the development of a method of synthesis by atomic layer deposition could allow to consider future application for this material in microelectronics. In fact, due to its inherent uniformity and conformity, atomic layer deposition (ALD) is currently envisaged as a solution to grow these sulfides on 200/300mm silicon wafers.

This presentation will describe for the first time the process developed for VS_2 synthesis on a 300mm silicon wafer. The different growth mechanisms involved with this film were first analyzed by *quasi-insitu* X-ray Photoelectron Spectroscopy (XPS) without airbreak. Also, the compositions were extracted to assess the growth rate and the incubation time and compared to other standard technics such as X-ray reflectometry. Subsequently, the physico-chemical properties of the film obtained by different will be presented. A focus on the optoelectronic properties of the film will be presented. Indeed, this film is transparent and conductive, an 8nm film has a transmittance of 78% and a resistivity of 784 µOhm.cm.

This work has been partially supported by the program EquipEx IMPACT (ANR-10-EQPX-33)

Keyword: *Quasi-insitu* XPS, Transition Metal Dichalcogenides, CVD.

4:20pm **2D+AP+EM+MI+NS+PS+TF-MoA-9 Controlled Growth of Transition Metal Dichalcogenide Monolayers for Applications in Nanoelectronic and Nanophotonic Devices***, A George, C Neumann, D Kaiser, R Mupparapu,* Friedrich Schiller University Jena, Germany*; U Hübner,* Leibniz Institute of Photonic Technology, Jena, Germany*; Z Tang, A Winter, I Staude, **Andrey Turchanin,*** Friedrich Schiller University Jena, Germany

Controlling the flow rate of precursors is highly essential for the growth of high quality monolayer crystals of transition metal dichalcogenides (TMDs) by chemical vapor deposition. Thus, introduction of an excess quantity of precursors affects the reproducibility of the growth process and results in the multilayer growth. Here, we demonstrate the use of Knudsen-type effusion cells for controlled delivery of sulfur precursor for the large area, high density, size-controlled and highly reproducible growth of monolayer TMD crystals [1]. The size of the grown crystals can be tuned between 10 - 200 µm. We grow MoS_2, WS_2, $MoSe_2$ and WSe_2 monolayer crystals as well as $MoSe_2$-WSe_2 lateral heterostructures and characterize them by optical microscopy, atomic force microscopy, Raman spectroscopy, photoluminescence spectroscopy and electrical transport measurements. It has been found that they possess a high crystalline, optical and electrical quality based on their single crystalline nature. We demonstrate their implementation in novel field-effect and nanophotonic devices and discuss an influence of the point defect density on their functional characteristics [2-3]. Moreover, we present a novel synthetic route for the integration of TMDs into lateral heterostructures with other 2D materials [4].

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4:40pm **2D+AP+EM+MI+NS+PS+TF-MoA-10 Atomic Layer Deposition of BN as a Novel Capping Barrier for B_2O_3***, **Aparna Pilli,*** J Jones, J Kelber,* University of North Texas*; A LaVoie, F Pasquale,* Lam Research Corporation

The deposition of boron oxide (B_2O_3) films on Si and SiO_2 substrates by atomic layer deposition (ALD) is of growing interest in microelectronics for shallow doping of high aspect ratio transistor structures. B_2O_3, however, forms volatile boric acid (H_3BO_3) upon ambient exposure, requiring a passivation barrier, for which BN was investigated as a possible candidate. Here, we demonstrate, deposition of BN by sequential BCl /NH reactions at 600 K on two different oxidized boron substrates: (a) B O deposited using BCl /H O ALD on Si at 300 K ("B O /Si"); and (b) a boron-silicon oxide formed by sequential BCl /O reactions at 650 K on SiO followed by annealing to 1000 K ("B-Si-oxide"). X-ray photoelectron spectroscopy (XPS) data demonstrate layer-by-layer growth of BN on B_2O_3/Si with an average growth rate of ~1.4 Å/cycle, accompanied by some B_2O_3 removal during the first BN cycle. In contrast, continuous BN growth was observed on B-Si-oxide without any reaction with the substrate. XPS data also indicate that the oxide/nitride heterostructures are stable upon annealing in ultrahigh vacuum to >1000 K. XPS data, after the exposure of these heterostructures to ambient, indicate a small amount of BN oxidation at the surface NH species, with no observable hydroxylation of the underlying oxide films. These results demonstrate that BN films, as thin as 13 Å, are potential candidates for passivating boron oxide films prepared for shallow doping applications.

5:00pm **2D+AP+EM+MI+NS+PS+TF-MoA-11 Atomic Layer Deposition of SiO_2 on Group VIII Metals: Towards Formation of a 2D Dielectric**, *T Suh, R Yalisove,* ***James Engstrom,*** Cornell University

The atomic layer deposition (ALD) of many metals, particularly Group VIII (now known as Groups 8, 9 and 10), on SiO_2 has been an active area of research in many fields, which include microelectronics and heterogeneous catalysis. There have been many fewer studies of the inverse—the deposition of SiO_2 on many of these same metals. One possible reason to explore the ALD growth of SiO_2 on transition metals is that it might provide a route to an atomically thick SiO_2 dielectric, *silicatene*. Silicatene is a 2D material that consists of a bilayer of Si_2O_3 linked to each other by bridging oxygen atoms (giving SiO_2), where there are no dangling bonds or covalent bonds to the underlying substrate on which it is grown. For example, an established route to form silicatene involves deposition of elemental Si in UHV and subsequent high-temperature annealing on various single-crystalline metal surfaces including, but not limited to, Ru(0001), Pt(111), and Pd(100). Such a process, unfortunately, is likely not compatible with high-volume manufacturing. With this motivation we embarked on a study of the plasma-assisted ALD of SiO_2 on e-beam deposited polycrystalline thin films of Ru, Pt and Pd using a commercial ALD reactor. We analyzed both the thin films and the starting substrates using a combination of techniques including contact angle, spectroscopic ellipsometry (SE) and X-ray photoelectron spectroscopy. Thin films of SiO_2 were deposited using tris(dimethylamido)silane and an oxygen plasma at a substrate temperature of 200 °C, and we examined growth for 5, 10, 20, 50 and 100 cycles. Contact angle measurements showed immediate evidence for SiO_2 deposition on all metal surfaces, and the contact angle decreased and remained constant and < 10° from 5 to 100 cycles of ALD. From SE we found little evidence of an incubation period, and growth was linear for the range of sample examined and the thickness deposited per cycle was remarkably constant at a value of 0.76-0.78 Å-cycle^{-1}. Analysis of these films using angle-resolved XPS was consistent with the formation of a thin film of SiO_2 with uniform thickness. Having characterized the thin film thickness-ALD cycle relationship we subjected SiO_2 thin films with thickness of ~ 7-15 Å to post-deposition high-temperature anneals in oxygen furnace. Initial attempts to form silicatene with an anneal at 800 °C, produced a structure suggesting possible interfacial reaction between the SiO_2 and Ru, perhaps involving silicide formation. We will end our presentation with a discussion of recent work involving a more extensive examination of the post-deposition annealing step, and deposition on patterned wafers.

Electronic Materials and Photonics Division
Room A214 - Session EM+PS+TF-MoA

New Devices and Materials for Logic and Memory

Moderators: Rehan Kapadia, University of Southern California, Nicholas Strandwitz, Lehigh University

1:40pm **EM+PS+TF-MoA-1 Short-term Plasticity to Long-term Plasticity Transition Mimicked by High Mobility InP FETs with TiO_2 Trapping Layer**, ***Jun Tao,*** *R Kapadia,* University of Southern California

Memory is widely believed to be encoded and stored in the central nervous system by altering the synapse strength via activity-dependent synaptic plasticity between millions of neurons in vertebrates. Consolidations from short-term plasticity (STP) to long-term plasticity (LTP) not only transform the important external stimuli to permanently stored information but release storage space for accepting new coming signals. Although memristor technology (e.g. RRAM) has been reported to mimic the STP and LTP characteristics and exhibited its merit in density comparing to traditional CMOS based SRAM technology, some conventional memristors suffer non-ideal operation speed, small dynamic range, and high resistance variation.

In our work, the single crystal Indium Phosphide (InP) based synaptic devices demonstrated its advantages not only in the emulation of the synaptic functions for both STP and LTP characteristics but also in the controllability of transition from STP to LTP. Since we interpret gate voltage pulses as the pre-synaptic action potentials, the source-drain current as post-synaptic current, and the channel conductance as synaptic weight, the consolidations from STP to LTP are elaborately demonstrated through mediating multiple action potential parameters like pulse numbers, pulse intervals (or rates), and pulse durations. The synaptic devices we demonstrated here are essentially single crystal channel InP Field Effect Transistors (FETs) fabricated on Si/SiO_2 substrates with the templated liquid-phase (TLP) method. In addition, TiO_2 trapping layer is inserted into the gate dielectric layer to provide extra deeper trap states. The 'ratchet' mechanism is utilized to have the charges 'fall' into the TiO_2 well and implement the transition from STP to LTP effectively.

2:00pm **EM+PS+TF-MoA-2 Magnetic Domain Wall Devices for Artificial Neural Network**, ***Saima Siddiqui,*** *S Dutta, A Tang, L Liu, M Baldo, C Ross,* MIT

Magnetic domain wall devices are promising candidates for logic [1] and storage class memory [2]. Due to the non-volatility and energy-efficient switching, this type of device is one of the prime candidates for in memory computing and brain-inspired computing. In-memory computing is a non-von-Neumann architecture where data computation and storage are done locally to reduce the data movement between the processor and the storage memory [3]. The layer-by-layer operations of data require synapses (i.e. variable resistors whose resistance vary linearly with the input) and activation function generators between layers (i.e. variable resistors whose resistance vary non-linearly with the input current).

Domain walls' motion in a magnetic wire is a function of applied current due to spin-orbit torque from an adjacent heavy metal (Fig. 1). The current density and spin orbit torque can be modified along the wire by adjusting the width of the heavy metal. The spin orbit torque then becomes a function of the domain wall position, which makes the domain wall motion a nonlinear function of the applied current (Fig. 2). Linear and nonlinear domain wall motion can be detected via magnetoresistance by using a magnetic tunnel junction in which the magnetic wire forms the free layer. The electrical detection is necessary for the analog matrix multiplication in neuromorphic accelerator. However, domain walls are pinned due to the magnetostatic energy minima on the sides of the MTJ. The synaptic (Fig. 3) and activation function (Fig 4) like magnetoresistive behavior can still be generated by using multiple MTJs in parallel. In this study, we demonstrate linear and nonlinear domain wall motion in magnetic wires and modify the design of magnetic tunnel junctions to convert these motions into magnetoresistance. The experimental observations of the device characteristics agree with both analytical and micromagnetic modeling.

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2:20pm **EM+PS+TF-MoA-3 Ferroelectric Devices for Non-von Neumann Computing**, *Z Wang,* ***Asif Khan,*** Georgia Institute of Technology **INVITED**

Excitation and inhibition go hand in hand in neuronal circuits in biological brains. For example, neurons in the visual and the auditory cortices provide excitatory responses to visual and auditory stimuli, respectively. On the other hand, interneurons in the central nervous system provide inhibitory signals to downstream neurons thereby imparting regulation and control in neuronal circuits—the loss of which often causes neurodegenerative disorders. These neuro-biological facts have inspired the bio-mimetic computational perspective that artificial, excitatory neurons need to be paired with inhibitory connections for functional correctness and efficient compute models such as spiking neural networks.

In this talk, we will introduce a ferroelectric neuromorphic transistor platform [1,2] which can (1) efficiently incorporate both excitatory and inhibitory inputs in the simple two transistor topology of an artificial, ferroelectric spiking neuron, and (2) emulate several classes of biological spiking dynamics (such as regular, fast, Thalamo-Cortical spiking and so on). We will discuss the recent experimental demonstrations of ferroelectric spiking neurons. The talk will end with a simulation experiment where a full-scale spiking neural network was implemented using experimentally calibrated ferroelectric circuit models and the network was benchmarked analog CMOS and other emerging device technologies.

References:

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3:00pm **EM+PS+TF-MoA-5 Ultrafast Measurement of Nanoseconds Polarization Switching in Ferroelectric Hafnium Zirconium Oxide***, **Mengwei Si**, P Ye,* Purdue University

Ferroelectric (FE) hafnium oxides (HfO$_2$) such as hafnium zirconium oxide (HZO) is the promising thin film ferroelectric material for non-volatile memory applications. The ultrafast measurements of polarization switching dynamics on ferroelectric (FE) and anti-ferroelectric (AFE) hafnium zirconium oxide (HZO) are studied, with the shortest electrical pulse width down to as low as 100 ps. The transient current during the polarization switching process is probed directly. The switching time is determined to be as fast as 10 ns to reach fully switched polarization with characteristic switching time of 5.4 ns for 15 nm thick FE HZO and 4.5 ns for 15 nm thick AFE HZO by Kolmogorov−Avrami−Ishibashi (KAI) model. The limitation by parasitic effect on capacitor charging is found to be critical in the correct and accurate measurements of intrinsic polarization switching speed of HZO. The work is in close collaborations with Xiao Lyu, Wonil Chung, Pragya R. Shrestha, Jason P. Campbell, Kin P. Cheung, Haiyan Wang, Mike A. Capano and was in part supported by SRC and DARPA.

3:20pm **EM+PS+TF-MoA-6 Interfacial Charge Engineering in Ferroelectric-Gated Mott Transistors***, X Chen, Y Hao, L Zhang, **Xia Hong**,* University of Nebraska-Lincoln

Ferroelectric field effect transistors (FeFETs) built upon Mott insulator channel materials have been intensively investigated over the last two decades for developing nonvolatile memory and logic applications with sub-nanometer size scaling limit. However, the intrinsically high carrier density of the Mott channel (10^{22}-10^{23}/cm^3) also imposes significant challenges in achieving substantial modulation of the channel conduction. In this work, we exploit the intricate interplay between interfacial charge screening and transfer effects in epitaxial heterostructures composed of two strongly correlated oxide layers, one layer of rare earth nickelate RNiO$_3$ (R = La, Nd, Sm) and one layer of (La,Sr)MnO$_3$ (LSMO), to realize a giant enhancement of the ferroelectric field effect in Mott-FeFETs with a Pb(Zr,Ti)O$_3$ gate. For devices with 1-5 nm single layer RNiO$_3$ channels, the room temperature resistance switching ratio (R_{off}-R_{on})/R_{on} increases with decreasing channel thickness till it reaches the electrical dead layer thickness. For devices built upon RNiO$_3$/LSMO bilayer channels, the resistance switching ratio is enhanced by up to two orders of magnitude compared with the single layer channel devices with the same channel thickness. Systematic studies of the layer thickness dependence of the field effect show that the LSMO buffer layer not only tailors the carrier density profile in RNiO$_3$ through interfacial charge transfer, but also provides an extended screening layer that reduces the depolarization effect in the ferroelectric gate. Our study points to an effective strategy for building high density nanoelectronic and spintronic applications via functional complex oxide heterointerfaces.

4:00pm **EM+PS+TF-MoA-8 The Interface of Transition Metal Dichalcogenides and Ferroelectric Oxides***, **Maria Gabriela Sales**, S Jaszewski, S Fields, R Christopher, N Shukla, J Ihlefeld, S McDonnell,* University of Virginia

Transition metal dichalcogenides (TMDs) are an interesting class of materials because of their unique properties owing to their 2D nature, wherein layers that are covalently bonded in-plane are held together by van der Waals forces in the out-of-plane direction, similar to graphene. However, unlike graphene, semiconducting TMDs have a band gap that is tunable with layer thickness, allowing control over its properties depending on specific applications. One such application is in ferroelectric-based transistors, which have high potential for use in memory and logic, but whose major drawback in integration is the poor semiconductor-ferroelectric interface when using silicon as the semiconducting channel, due to issues such as interdiffusion across the interface. Thus, a promising alternative route is using a TMD as the channel with a ferroelectric material as the gate dielectric. This is expected to have an improved interface quality because of the fact that TMDs have no dangling bonds at the surface and are highly stable in-plane. In this study, we focus on a mixture of hafnium oxide and zirconium oxide as our ferroelectric material, with zirconium stabilizing the ferroelectric phase in hafnia. We explore the TMD/ferroelectric structure, addressing certain integration issues in growth, and looking at their interface chemistry and thermal stability. Specifically, we look at commercially available geological MoS$_2$ and molecular beam epitaxy-grown WSe$_2$ interfaced with an atomic layer deposited Hf$_x$Zr$_{1-x}$O$_2$ ferroelectric. Our report will focus on the results of our investigations of this interface carried out using a combination of X-ray photoelectron spectroscopy (XPS) and X-ray diffraction (XRD) techniques.

4:20pm **EM+PS+TF-MoA-9 Electronic and Thermal Properties of 2D Materials***, **Connor McClellan**, E Yalon, K Smithe, C English, S Vaziri, C Bailey, A Sood, M Chen, E Pop,* Stanford University

This talk will present recent highlights from our research on two-dimensional (2D) materials and devices including graphene, and transition metal dichalcogenides (TMDs). The results span from fundamental measurements and simulations, to devices, to system-oriented applications which take advantage of unusual 2D material properties.

Using the low cross-plane thermal conductance, we found unexpected applications of graphene as an ultra-thin electrode to reduce power consumption in phase-change memory [1]. We have also demonstrated wafer-scale graphene systems for analog dot product computation [2]. We have grown monolayer 2D semiconductors by chemical vapor deposition over cm^2 scales on amorphous oxides, including MoS$_2$ with low device variability [3], WSe$_2$, and MoSe$_2$.

Using a self-aligned process, we demonstrated 10 nm gate-length monolayer MoS$_2$ transistors with excellent switching characteristics and approaching ballistic limits [4]. Using sub-stochiometric oxides, we achieved high electron doping to reduce electrical contact resistance down to 480 Ω·µm and increase on-current up to a record of 700 µA/µm in monolayer MoS$_2$ [5]. We also directly measured the saturation velocity in monolayer MoS$_2$, finding it is thermally-limited (i.e. by device self-heating and phonon scattering) to about one-third that of silicon and about one-tenth that of graphene [6]. Using Raman thermometry, we uncovered low thermal boundary conductance (~15 MW/m^2/K) between MoS$_2$ and SiO$_2$, which could limit heat dissipation in 2D electronics [7]. We are presently exploring unconventional applications including thermal transistors [8], which could enable nanoscale control of heat in "thermal circuits" analogous with electrical circuits. These studies reveal fundamental limits and new applications of 2D materials, taking advantage of their unique properties.

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4:40pm **EM+PS+TF-MoA-10 Electronics in Flatland***, **Sanjay Banerjee**,* University of Texas at Austin **INVITED**

2D materials such as graphene, transition metal dichalcogenides and topological insulators have opened up avenues in beyond-CMOS device concepts. We will discuss our work involving single or many-particle 2D-2D tunneling, leading to transistors with negative differential resistance. We also explore spintronics in these systems for novel logic and memory devices. We will also discuss the use of these materials in less esoteric, but more practical high frequency, mechanically flexible FETs for IoT applications.

Plasma Science and Technology Division
Room B130 - Session PS+AS+EM+SS+TF-MoA

Plasma-Surface Interactions

Moderators: Sebastian Engelmann, IBM T.J. Watson Research Center, Sumit Agarwal, Colorado School of Mines

1:40pm **PS+AS+EM+SS+TF-MoA-1 Cleaning Chamber Walls after ITO Plasma Etching Process***, **Salma Younesy**, C Petit-Etienne,* LTM/CNRS, France*; S Barnola,* CEA-LETI, France*; P Gouraud,* ST Microelectronics, France*; G Cunge,* LTM/CNRS, France

Controlling the reactor walls in plasma etching is a key to avoid process drifts. In fact, the deposition of plasma generated species on the reactor walls during etching changes their chemical nature, thereby affecting plasma characteristics such as the radical concentration and the ion flux, which eventually leads to etch rates, anisotropy and selectivity variations. To overcome this issue, the chemical nature of the deposit formed on the chamber walls during etching must be determined to be able to develop efficient plasma chamber cleaning strategies. For new optoelectronic devices, the integration of materials with low volatility etch products such as ITO renders the dry cleaning processes long and laborious. Therefore, we have investigated several plasma chemistries to find out the most efficient reactor cleaning strategy after ITO etching.

The chemical nature of the reactor walls is analyzed quasi in situ by XPS using the “floating sample” technique [1], in which an Al_2O_3 sample representing the reactor walls is fixed on the 200 mm diameter wafer, but separated from it by a 4 mm gap (which forces the sample to be electrically floating even when the holding wafer is RF-biased). After the process, the wafer and sample can be transported under vacuum to the XPS analyzer and the coating formed on the walls can be analyzed (along with the cleaning efficiency).

The results show that after ITO etching the walls are contaminated by indium. At low temperature, BCl_3/Cl_2 plasma is ineffective to remove this deposit while HBr/Ar and CH_4/Cl_2 chemistries provide promising results. More particularly, an Ar-rich mixture of HBr/Ar is the most efficient strategy, which suggests that Ar^+ ions play an important role in the removal of ITO etching deposit.

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2:00pm **PS+AS+EM+SS+TF-MoA-2 Plasma Resistance of Sintered Yttrium Oxyfluoride (YOF) with Various Y, O, and F Composition Ratios***, **Tetsuya Goto**, Y Shiba, A Teramoto,* Tohoku University, Japan*; Y Kishi,* Nippon Yttrium Co., Ltd, Japan*; S Sugawa,* Tohoku University, Japan

Yttrium oxyfluoride (YOF) has been received much attention as the material for various functional components used in the plasma process chamber for semiconductor manufacturing. This is because, as compared to the widely used Y_2O_3, YOF is stable against various corrosive plasmas using halogen gases which is frequently used in the etching processes and/or chamber cleaning processes. We have reported that YOF (1:1:1) film has the higher resistance to various plasma conditions (N_2/Ar, H_2/Ar, NH_3/Ar, NF_3/Ar, O_2/Ar) than the Y_2O_3 and YF_3 films [1, 2]. In this presentation, we report the effect of ion bombardment on the surface structure of sintered yttrium oxyfluoride (YOF) with various Y, O, and F composition ratios. By combining the starting materials of YOF, $Y_5O_4F_7$, and YF_3 in sintering, the YOF samples with different Y, O, and F composition ratios were prepared. In these samples, the oxygen composition ratio was changed from 33 at% to 7at%. According to this, the fluorine composition ratio was changed from 33at% to 66at%, and thus, the samples became from Y_2O_3 rich to YF_3 rich. Ar ion beam with 500 eV was irradiated to these YOF samples. It was found that the sputtering etching rate was monotonically decreased as the oxygen composition ratio was decreased. It was also found that the surface roughness was relatively smaller for the samples with the composition ratios of Y:O:F=1:1:1 and 5:4:7 (both correspond to the stable composition) than those with other composition ratios. The results indicated that the atomic composition ratio is an important parameter to obtain YOF with good stability against plasmas.

Acknowledgement

The plasma irradiation and inspection were carried out in Fluctuation-Free-Facility in Tohoku University.

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2. A. Teramoto, Y. Shiba, T. Goto, Y. Kishi and S. Sugawa p. 16, AVS 65th International Symp., Long Beach, 2019.

2:20pm **PS+AS+EM+SS+TF-MoA-3 Understanding Atomic Layer Etching: Thermodynamics, Kinetics and Surface Chemistry***, **Jane P. Chang**[1],* University of California, Los Angeles **INVITED**

The introduction of new and functionally improved materials into silicon based integrated circuits is a major driver to enable the continued down-scaling of circuit density and performance enhancement in analog, logic, and memory devices. The top-down plasma enhanced reactive ion etching has enabled the advances in integrated circuits over the past five decades; however, as more etch-resistive materials are being introduced into these devices with more complex structures and smaller features, atomic level control and precision is needed in selective removal of these materials. These challenges point to the growing needs of identifying and developing viable etch chemicals and processes that are more effective in patterning complex materials and material systems such as multiferroics, magnetic materials and phase change materials, with tailored anisotropy and selectivity.

In this talk, a universal chemical approach is presented, combining thermodynamic assessment and kinetic validation to identify and validate the efficacy of various plasma chemistries. Specifically, potential reactions between the dominant vapor phase/condensed species at the surface are considered at various temperatures and reactant partial pressures. The volatility of etch product was determined to aid the selection of viable etch chemistry leading to improved etch rate of reactive ion etching process. Based on the thermodynamic screening, viable chemistries are tested experimentally to corroborate the theoretical prediction. Some of the above mentioned material systems such as complex oxides and metallic material systems used in logic and memory devices are used as examples to demonstrate the broad applicability of this approach.

3:00pm **PS+AS+EM+SS+TF-MoA-5 Comparison of Silicon Surface Chemistry between Photo-Assisted Etching and Ion-Assisted Etching***, **Emilia Hirsch**, L Du, V Donnelly, D Economou,* University of Houston

Etching of p-Si in 60 mTorr Cl_2/Ar Faraday-shielded inductively coupled plasmas was investigated under both ion-assisted etching (IAE) and photo-assisted etching (PAE) conditions. Real-time etching rate and after-etch Si surface chemical composition were characterized by laser interferometry and vacuum-transfer X-ray photoelectron spectroscopy (XPS), respectively. By varying the duty cycle of a pulsed negative DC bias applied to the sample stage, it was found that the IAE rate scaled with the ion current integrated over the bias period, and the total etching rate was simply the sum of PAE and IAE rates. Consequently, little or no synergism occurred between VUV photon- and ion-bombardment stimulated etching. The PAE rate was ~ 210 nm/min at 60 mTorr. Above the 25 eV threshold, the IAE etching rate increased with the square root of the ion energy. Compared to RF bias, a more monoenergetic IED was obtained by applying pulsed DC bias, allowing precise control of ion energy near the low-energy IAE threshold. XPS spectra showed that, when compared to IAE, the chlorinated layer on the surface of samples etched under PAE conditions had significantly lower chlorine content, and it was composed of SiCl only. Under IAE conditions, however, Si· dangling bonds, $SiCl_2$, and $SiCl_3$ were found, in addition to SiCl, with relative abundance of $SiCl>SiCl_2>SiCl_3$. The absence of higher chlorides and Si· dangling bonds under PAE conditions suggested that VUV photons and ions are interacting with the Si surface very differently. When PAE and IAE occurred simultaneously, energetic ion bombardment dictated the surface chemistry that resulted in the formation of higher chlorides.

3:20pm **PS+AS+EM+SS+TF-MoA-6 Chemical Reaction Probabilities in the Etching of Si by Fluorine Atoms Produced in a Mixture of $NF\text{-}_3/SF_6$ Plasma***, **Priyanka Arora**[2], T Nguyen,* University of Houston*; S Nam,* Samsung Electronic Company, Republic of Korea*; V Donnelly,* University of Houston

Reaction probabilities in the absence of ion bombardment, defined as the number of silicon atoms removed per incident fluorine atom, have been investigated in mixtures of NF_3 and SF_6 plasmas in an inductively-coupled plasma reactor. Fluorine atom densities were measured by optical emission actinometry, and isotropic etching rates were measured by the degree of undercutting of SiO_2-masked silicon, using cross-sectional scanning electron microscopy (SEM). In addition, atomic force microscopy (AFM) was used to examine surface roughness after etching. The F atom reaction probabilities derived from these measurements indicate ~30-fold higher reaction probability in SF_6 plasma compared with values in NF_3 plasma. Surfaces etched in SF_6 plasma were much smoother than those etched in NF_3 plasma. Addition of only 10% SF_6 to an NF_3 plasma produced a much higher reaction probability (~10-fold) than in a pure NF_3 plasma. This surprising enhancement of reaction probabilities for F with Si in SF_6 plasma will be shown to be due to adsorbed sulfur acting as a catalyst to greatly enhance the etching rate of Si. By allowing sulfur in isopropyl alcohol to evaporate on the masked Si samples, sulfur could be preferentially deposited in relatively high concentrations near mask edges in ~2 mm diameter periodic “strings of beads”. When this sample is placed side by side with one not exposed to sulfur, the sulfur dosed sample etched several times faster at the center of each bead, while sulfur-free surface exhibited the expected slower rate.

4:00pm **PS+AS+EM+SS+TF-MoA-8 John Thornton Memorial Award Lecture: Low Temperature Plasma-Materials Interactions: Foundations of Nanofabrication And Emerging Novel Applications At Atmospheric Pressure***, **Gottlieb S. Oehrlein**[3],* University of Maryland, College Park **INVITED**

Our ability to understand and control the interactions of non-equilibrium plasma with surfaces of materials has been an exciting frontline and

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[1] **PSTD Plasma Prize Winner**

[2] **Coburn & Winters Student Award Finalist**

[3] **John A. Thornton Memorial Award Winner**

enabled the realization of new applications and technologies. The plasma-surface interactions (PSI) field has grown rapidly because of a number of reasons. First, plasma-assisted etching (PE) is one of the foundations of micro- and nanofabrication where increasingly atomistic precision in materials processing is required. By enabling the realization of intricate material features that semiconductor circuits and microstructures consist of, PE makes possible our technological tools that form modern society. This exceedingly complex procedure begins with the transfer of a resist mask in a directional and chemically selective fashion into various materials. Controlling profile shape, critical dimensions, surface roughness, and electrical integrity are crucial, and determined by PSI. Second, development of novel low temperature plasma sources operating at atmospheric pressure has enabled advances in areas where use of PSI has historically been limited, e.g. biology. In this talk I will present a brief review of contributions that I and my collaborators have been honored to make to our understanding of PSI, in particular in the areas of surface processes that are essential for achieving the objectives of plasma etching processes in current semiconductor fabrication that are approaching the atomic scale, and interaction of low temperature atmospheric pressure plasma sources with model polymers and biomolecules aimed at disinfection and sanitation of biological materials.

4:40pm **PS+AS+EM+SS+TF-MoA-10 Determining Surface Recombination Probabilities during Plasma-enhanced ALD using Lateral High Aspect Ratio Structures***, **Karsten Arts,*** Eindhoven University of Technology, The Netherlands, Netherlands*; M Utriainen,* VTT Technical Research Centre of Finland, Finland*; R Puurunen,* Aalto University School of Chemical Engineering, Finland*; E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands*; H Knoops,* Eindhoven University of Technology, The Netherlands

In this work we measure surface recombination probabilities *r* of plasma radicals, which is essential for the modeling and understanding of radical-driven plasma processes. Such quantitative information on *r* is scarcely reported in the literature and typically obtained by difficult and indirect measurement techniques. Here, we determine *r* using plasma-enhanced atomic layer deposition (ALD) on high aspect ratio (AR) structures, where the AR up to which film growth is obtained gives direct insight into *r* corresponding to the growth surface. This is demonstrated by measuring the recombination probabilities of O atoms on $SiO\text{-}_2$, TiO_2, Al_2O_3 and HfO_2, revealing a surprisingly strong material-dependence. Aside from studying different materials, our method can for instance be used to investigate the impact of pressure and temperature on *r*. This can provide valuable information for e.g., device fabrication, plasma source design and simulations, in the context of plasma-enhanced ALD but also relevant outside this field.

For this study, we use microscopic lateral-high-aspect-ratio (LHAR) structures[1] supplied by VTT (PillarHall® LHAR4). These chips have extremely high AR trenches (AR<10000) such that film growth is limited up to a certain penetration depth for even the most conformal processes. In the case of plasma ALD, where the film conformality is typically limited by surface recombination,[2] we show that the achieved penetration depth can be used to determine *r*. Furthermore, the LHAR structures allow for comparison of growth behavior with and without an ion component.

These opportunities are demonstrated by plasma ALD of $SiO\text{-}_2$, TiO_2, Al_2O_3 and HfO_2, using an O_2/Ar plasma and $SiH_2(N(C_2H_5)_2)_2$, $Ti(N(CH_3)_2)_4$, $Al(CH_3)_3$ and $HfCp(N(CH_3)_2)_3$, respectively, as precursors. It is observed that an exponential increase in plasma exposure time is required to linearly increase the film penetration depth. This relation, which solely depends on *r*, has been used to determine $r=(6\pm2)\cdot10^{-5}$, $(6\pm3)\cdot10^{-5}$, $(1\text{-}10)\cdot10^{-3}$ and $(0.1\text{-}10)\cdot10^{-2}$ for oxygen radicals on $SiO\text{-}_2$, TiO_2, Al_2O_3 and HfO_2, respectively. Corresponding to these large differences in *r*, growth of SiO_2 and TiO_2 penetrated extremely deep up to AR~900, while deposition of Al_2O_3 and HfO_2 was achieved up to AR~90 and AR~40, respectively. This strong material-dependence illustrates the importance of our quantitative research on surface recombination of plasma radicals.

1. Arts, Vandalon, Puurunen, Utriainen, Gao, Kessels and Knoops, J. Vac. Sci. Technol. A **37**, 030908 (2019)
2. Knoops, Langereis, van de Sanden and Kessels, J. Electrochem. Soc. **157**, G241 (2010)

5:00pm **PS+AS+EM+SS+TF-MoA-11 Study of Plasma-Photoresist Interactions for Atomic Layer Etching Processes***, **Adam Pranda**[1], K Lin, G Oehrlein,* University of Maryland, College Park

The emergence of atomic layer etching (ALE) processes has enabled improved control of surface profiles. Whereas the implementation of ALE processes on hard mask materials has been well established, the effects of these processes on photoresist materials is not well known. With the advent of next generation extreme ultraviolet (EUV) photoresists, there is the potential to utilize ALE processes with photoresist materials for fabrication of sub-10 nm feature sizes.

The plasma processing of photoresist materials induces several key physical and chemical modifications which affect material properties such as the etching behavior and surface roughness. In this work, we utilize in-situ ellipsometry, atomic force microscopy (AFM), x-ray photoelectron spectroscopy (XPS), and Fourier transform infrared (FTIR) spectroscopy to interpret the relationships between the aforementioned material properties, the photoresist chemical composition, and plasma ALE parameters such as ion energy and precursor gas type. By comparing these relationships between baseline continuous plasma etching processes and ALE processes, which include the introduction of chemically reactive surface passivation, we elucidate the intrinsic photoresist behaviors under plasma exposure and how an ALE process specifically impacts these behaviors.

Under nonreactive plasma chemistries, a universal response among photoresist materials is the development of a surface dense amorphous carbon (DAC) layer due to energetic ion bombardment. We have found that the photoresist etch rate is inversely proportional to the DAC layer thickness.[1] However, photoresists with UV sensitive pendant groups, such as 193 nm photoresists, develop a greater surface roughness due to the stresses in the surface generated by synergistic ion and UV photon interactions.

With depositing fluorocarbon (FC)-based ALE gas chemistries, the deposited FC layer reacts with the DAC layer and converts it into a mixed layer. This incorporation of FC into the DAC layer reduces the surface roughness without impacting the etch rate of the underlying photoresist as long as a sufficient DAC layer thickness remains.[2] This behavior is potentially advantageous for maximizing the photoresist to SiO_2 selectivity while maintaining an adequate surface roughness.

The authors acknowledge S.A. Gutierrez Razo, J.T. Fourkas, R.L. Bruce, S. Engelmann, and E.A. Joseph for collaborations on aspects of this work, and financial support by the National Science Foundation (NSF CMMI-1449309) and Semiconductor Research Corporation (2017-NM-2726).

[1] A. Pranda et al., J. Vac. Sci. Technol. A **36**, 021304 (2018).

[2] A. Pranda et al., Plasma Process. Polym. e1900026 (2019).

Materials and Processes for Quantum Information, Computing and Science Focus Topic

Room B231-232 - Session QS+EM+MN+NS+VT-MoA

Systems and Devices for Quantum Computing

Moderators: Jonas Bylander, Chalmers University of Technology, Sweden, Ruichen Zhao, National Institute of Standards and Technology (NIST)

1:40pm **QS+EM+MN+NS+VT-MoA-1 DEMUXYZ Gate Using Single Microwave Drive Line for Multiple Qubits***, **Matteo Mariantoni,*** University of Waterloo, Canada*; C Earnest,* University atof Waterloo, Canada*; J Béjanin,* Unversity of Waterloo, Canada

Superconducting qubits have the potential to lead to large-scale quantum computers with 10^5 or more qubits in 2D arrays. As the number of qubits increases, finding methods to connect all the necessary control lines to each qubit can become a serious challenge. In this talk, we introduce a new demultiplexed one-qubit gate: DEMUXYZ. This gate makes it possible to decrease the number of microwave control lines from N^2 to 1 by allowing multiple qubits to share a single microwave line. The shared line carries a continuous wave (CW) microwave tone, which is initially detuned from the qubits' idle frequency. When a qubit must undergo an arbitrary rotation on the Bloch sphere, the qubit is tuned on resonance with the CW tone and allowed to interact with the drive for the duration required to achieve the desired rotation. The rotation phase is tuned by detuning the qubit frequency away from the drive and idle frequency for the required time

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[1] **Coburn & Winters Student Award Finalist**

length. We demonstrate a first proof of concept for this gate performing experiments on Xmon transmon qubits. We characterize the gate ON/OFF ratio and perform quantum state tomography.

Funding Acknowledgement: This research was undertaken thanks in part to funding from the Canada First Research Excellence Fund (CFREF) and the Discovery and Research Tools and Instruments Grant Programs of the Natural Sciences and Engineering Research Council of Canada (NSERC).

2:00pm **QS+EM+MN+NS+VT-MoA-2 Structural and Electronic Characterization of a Novel Si/SiGe Heterostructure for Quantum Computing***, Thomas McJunkin*, *E MacQuarrie, S Neyens, B Thorgrimsson, J Corrigan, J Dodson, D Savage, M Lagally, R Joynt, M Friesen, S Coppersmith, M Eriksson,* University of Wisconsin - Madison

In recent years, silicon-based quantum dots have been shown to be a promising avenue for quantum computing. However, dots formed in silicon quantum wells exhibit a near-degeneracy of the two low-lying valley states. Motivated by a desire to increase the magnitude and tunability of this valley splitting, we report the characterization of a novel Si/SiGe heterostructure grown with a thin layer of SiGe embedded within the Si quantum well, near the top of the well. The Si/SiGe heterostructure is grown via UHV-CVD on a linearly graded SiGe alloy with a final Ge concentration of 29%. STEM measurements reveal the quantum well structure to consist of a ~10 nm Si layer, followed by a thin ~1 nm SiGe layer, and subsequent ~2 nm layer of pure Si. Above this quantum well, a ~35 nm layer of SiGe with 29% Ge is grown to separate the quantum well from the surface. The intent of this ~1 nm layer of SiGe, positioned just below the upper interface of the quantum well, is to modify the valley splitting of electrons in a 2-dimensional electron gas (2DEG) that reside near this interface. By modifying an external vertical electric field, the electron wavefunction can be moved on and off this spike in germanium concentration.

We report electronic measurements of both Hall bars and quantum dot devices that are fabricated on this heterostructure. Shubnikov-de Haas (SdH) and quantum Hall (QH) measurements reveal a peak transport mobility in excess of 100,000 $cm^2/(V s)$ at 6 x 10^{11} cm^{-2} carrier density . We report SdH and QH measurements over a wide range of carrier density and magnetic field in the form of a fan diagram. Valley splitting values are measured in the quantum dot device by magnetospectroscopy, in which a few-electron dot transition is measured as the in-plane magnetic field is swept. Measuring at the second, third, and fourth electron transition in the quantum dot, we find valley splittings of 29, 48, and 65 ueV, respectively. To measure tunability of valley splitting, nearby gate voltages are changed to vary the vertical electric field at constant charge occupation. We find that both the lowest lying valley splitting and the valley splitting in the first excited orbital can be tuned over a factor of 2 by means of such changes in gate voltage.

2:20pm **QS+EM+MN+NS+VT-MoA-3 Efficient Quantum Computation using Problem-specific Quantum Hardware and Algorithms***, Stefan Filipp,* IBM Research - Zurich, Switzerland **INVITED**

In recent years we have observed a rapid development of quantum technologies for the realization of quantum computers that promise to outperform conventional computers in certain types of problems. This includes problems in optimization, machine learning, finite element calculations, and in the computation of complex molecules. A key requirement to perform computations on current and near-term quantum processors is the design of quantum algorithms with short circuit depth that finish within the coherence time of the qubits. To this end, it is essential to implement a set of quantum gates that are tailored to the problem at hand and that can be directly implemented in hardware. To efficiently compute the ground and excited states of molecular hydrogen we utilize a parametrically driven tunable coupler to realize exchange-type gates that are configurable in amplitude and phase on two fixed-frequency superconducting qubits. Such gates are particularly well suited for quantum chemistry applications because they preserve the number of qubit excitations corresponding to the fixed number of electrons in the molecule. With gate fidelities around 95% we compute the eigenstates within an accuracy of 50 mHartree on average, an good starting point for the simulation of larger molecular systems.

3:00pm **QS+EM+MN+NS+VT-MoA-5 Reconfigurable Magnetic Textures for Quantum Information Applications***, Alex Matos-Abiague,* Wayne State University **INVITED**

Spintronic devices such as spin valves have extensively been used for non-volatile memory applications. The magnetic fringe fields generated by spin valves strongly depend on the magnetic state of the device. Thus, an array of electrically switchable spin valves allows for the generation of reconfigurable magnetic textures whose specific form and properties can be controlled on the nanometer scale. When combined with materials with large g-factor, such magnetic textures can have sizable effects not only on the spin but also on the localization, exchange, and transport properties of carriers. We show how the local control of the fringe-field-generated magnetic texture provides a unique tool for creating effective reconfigurable nanostructures and how it can be used for various quantum information applications. In particular, we focus on the use of reconfigurable magnetic textures as a new path to the realization of fault-tolerant topological quantum computing by enabling the generation and manipulation of Majorana bound states (MBSs) in superconductor/semiconductor heterostructures [1-4]. MBSs are emergent quasiparticles that obey non-Abelian statistics and can store quantum information that is immune against smooth local perturbations. Magnetic textures can provide not only synthetic spin-orbit and Zeeman fields -two important ingredients for the creation of MBSs- but also spatial confinement by creating closed domains in the form of effective topological wires. The effective wires can be re-shaped and re-oriented by properly changing the magnetic texture, allowing for the transportation of the MBSs [1,3] and the realization of quantum gates through braiding operations [2]. Other platforms combining the use of reconfigurable magnetic textures and Josephson junctions, as well as the main experimental challenges regarding materials, scalability, and detection are also discussed.

ACKNOWLEDGMENTS: This work is supported by DARPA Grant No.DP18AP900007 and US ONR Grant No. N000141712793

[1] G. L. Fatin, A. Matos-Abiague, B. Scharf, I Žutić, Phys. Rev. Lett. **117**, 077002 (2016).

[2] A. Matos-Abiague, J. Shabani, A. D. Kent, G. L. Fatin, B. Scharf, I. Žutić, Solid State Commun. **262**, 1 (2017).

[3] T. Zhou, N. Mohanta, J. E. Han, A. Matos-Abiague, and I. Žutić, Phys. Rev. B **99**, 134505 (2019).

[4] N. Mohanta, T. Zhou, J. Xu, J. E. Han, A. D. Kent, J. Shabani, I. Žutić, and A. Matos-Abiague, arXiv:1903.07834

4:00pm **QS+EM+MN+NS+VT-MoA-8 Coaxial Multilayer Superconducting Circuits for Quantum Computing***, Peter Leek,* University of Oxford, UK **INVITED**

Superconducting circuits are one of the leading candidates for the realization of quantum computers, in particular for near-term applications which may already be reached with circuits consisting of a few hundred qubits, provided they are operated at high fidelity. Until recently, the topology of superconducting circuits has typically been constrained to two dimensions, which becomes difficult to scale as the number of qubits increases and control and measurement wiring is needed for qubits in the middle of large arrays. It is natural to explore new circuit topologies that incorporate wiring in the third dimension to solve this problem. In this talk I will present an overview of an approach that builds on a coaxially-symmetric circuit QED unit cell with out-of-plane wiring [1] that provides a simple route to scaling to grids of many qubits. In this approach, arrays of qubits and resonators can be fabricated on opposing sides of a substrate and capacitively coupled, while control and readout are achieved via off-chip coaxial wires which run perpendicular to the chip plane and are built into a precision micro-machined enclosure that provides a high-quality microwave environment for the circuit.

[1] Rahamim et al., Applied Physics Letters **110**, 222602 (2017)

4:40pm **QS+EM+MN+NS+VT-MoA-10 Josephson Parametric Amplifiers based on Micron Scale Overlap Junctions (O-JPA)***, Mustafa Bal, J Long, R Zhao, H Wang,* National Institute of Standards and Technology (NIST)*; C McRae,* National Institute of Standards and Technology (NIST) and University of Colorado Boulder*; R Lake, X Wu, H Ku, D Pappas,* National Institute of Standards and Technology (NIST)

Quantum limited amplifiers have become indispensable tools in superconducting quantum circuits. In recent years, quantum limited amplification has been demonstrated in parametric amplifiers based on high kinetic inductance superconductors as well as Josephson junctions. Previously, we have demonstrated submicron scale overlap Josephson junction fab process for qubits with long coherence times [1]. Here, we extend the overlap junction fab process to micron scale junctions to enable the realization of other superconducting quantum devices such as overlap junction-based Josephson parametric amplifiers (O-JPA). Our fab scheme yield frequency tunable O-JPAs with negligible insertion loss. We readily observe over 25 dB gain. Compared to other competing processes, overlap junction process for micron scale junctions allows the fabrication of O-JPAs with high yield and good device performance at a much lower infrastructure requirements. The fabrication details of overlap junction process as well as the results of O-JPA characterization will be presented. The metrology of overlap Josephson junctions will also be presented in this this symposium [2].

[1] X. Wu, J. L. Long, H. S. Ku, R. E. Lake, M. Bal, and D. P. Pappas, "Overlap junctions for high coherence superconducting qubits", Appl. Phys. Lett. **111**, 032602 (2017).

[2] R. Zhao *et al.*, "Josephson Junction metrology for superconducting quantum device design", also presented at AVS 66th International Symposium & Exhibition.

5:00pm **QS+EM+MN+NS+VT-MoA-11 Development and Characterization of a Flux-pumped Josephson Parametric Amplifier***, Martina Esposito,* University of Oxford, UK

Josephson parametric amplification is a tool of paramount importance in circuit quantum electrodynamics (circuit-QED), especially for the quantum-noise-limited single-shot readout of superconducting qubits. Here we present the development and characterization of a flux-pumped Josephson parametric amplifier (JPA) based on a lumped-element LC resonator, in which the inductance L is composed by a geometric inductance and an array of superconducting quantum interference devices (SQUIDs) [1]. In addition, we show preliminary experiments where the JPA is used as the first stage of amplification for the readout of a superconducting qubit based on a coaxial architecture recently developed in our lab in Oxford [2]. Finally, we will introduce future scientific direction based on using JPAs for generation and control of non-classical states in microwave photons.

[1] M. Esposito et al. EPJ Web of Conferences 198, 00008 (2019)

[2] J. Rahamim et al. Applied Physics Letters 110, 222602 (2017)

2D Materials
Room A226 - Session 2D+EM+MI+MN+NS+QS-TuM

Novel Quantum Phenomena

Moderator: Arend van der Zande, University of Illinois at Urbana Champaign

8:00am **2D+EM+MI+MN+NS+QS-TuM-1 Charge Density-Wave States in Single-Layer Transition-Metal Dichalcogenides***, **Phil King**,* University of St Andrews, UK **INVITED**

Control over materials thickness down to the single-atom scale has emerged as a powerful tuning parameter for manipulating not only the single-particle band structures of solids, but increasingly also their interacting electronic states and phases. A particularly attractive materials system in which to explore this is the transition-metal dichalcogenides, both because of their naturally-layered van der Waals structures as well as the wide variety of materials properties which they are known to host. Yet, how their interacting electronic states and phases evolve when thinned to the single-layer limit remains a key open question in many such systems. Here, we use angle-resolved photoemission to investigate the electronic structure and charge density wave (CDW) phases of monolayer $TiSe_{2,}$ $TiTe_2$, and VSe_2. Three-dimensionality is a core feature of the electronic structure of all of these parent compounds, but we show how their CDW phases not only persist, but are strengthened, in the monolayer limit. In $TiSe_2$, we observe an orbital-selective CDW, necessarily without a k_z-selectivity in band hybridisation that is of key importance for the bulk instability,[1] while $TiTe_2$ is driven into a charge-ordered phase in the monolayer which is not stable in the bulk at all. In VSe_2, we show how the monolayer hosts a much stronger-coupling CDW instability than the bulk, which in turn drives a metal-insulator transition, removing a competing instability to ferromagnetism.[2] Together, these studies point to the delicate balance that can be realized between competing interacting states and phases in monolayer transition-metal dichalcogenides.

This work was performed in close collaboration with M.D. Watson, A. Rajan, J. Feng, D. Biswas, and colleagues from the Universities of St Andrews, Oxford, Keil, Diamond, Elettra, and SOLEIL.

[1] Watson *et al.*, Phys. Rev. Lett. 122 (2019) 076404.

[2] Feng *et al.,* Nano Lett. 18 (2018) 4493.

8:40am **2D+EM+MI+MN+NS+QS-TuM-3 Sublattice Symmetry Breaking and Kondo-effect Enhancement in Strained Graphene***, D Zhai,* Ohio University*; K Ingersent,* University of Florida*; S Ulloa, **Nancy Sandler**,* Ohio University

Kondo physics in doped monolayer graphene is predicted to exhibit unusual features due to the linear vanishing of the pristine material's density of states at the Dirac point. Despite several attempts, conclusive experimental observation of the phenomenon remains elusive. One likely obstacle to identification is a very small Kondo temperature scale *TK* in situations where the chemical potential lies near the Dirac point. We propose tailored mechanical deformations of monolayer graphene as a means of revealing unique fingerprints of the Kondo effect. Inhomogeneous strains are known to produce specific alternating changes in the local density of states (LDOS) away from the Dirac point that signal sublattice symmetry-breaking effects. Small LDOS changes can be amplified in an exponential increase or decrease of *TK* for magnetic impurities attached at different locations. We illustrate this behavior in two deformation geometries: a circular "bubble" and a long fold, both described by Gaussian displacement profiles. We calculate the LDOS changes for modest strains and analyze the relevant Anderson impurity model describing a magnetic atom adsorbed in either a "top-site" or a "hollow-site" configuration. Numerical renormalization-group solutions of the impurity model suggest that higher expected *TK* values, combined with distinctive spatial patterns under variation of the point of graphene attachment, make the top-site configuration the more promising for experimental observation of signatures of the Kondo effect. The strong strain sensitivity of *TK* may lift top-site Kondo physics into the range experimentally accessible using local probes such as scanning tunneling microscopy.

9:00am **2D+EM+MI+MN+NS+QS-TuM-4 Indirect Transition and Opposite Circular Polarization of Interlayer Exciton in a MoSe2 WSe2 van der Waals Heterostructure***, **Hsun-Jen Chuang**, A Hanbicki, M Rosenberger, C Hellberg, S Sivaram, K McCreary, I Mazin, B Jonker,* U.S. Naval Research Laboratory

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). One unique new optical property of heterostructure is an interlayer exciton (ILE), a spatially indirect, electron-hole pair with the electron in one TMD layer and the hole in the other. Here, we fabricated MoSe2/WSe2 hetero-bilayer encapsulated in h-BN with the alignment angle close to 60 degree between MoSe2 and WSe2. Followed by the state-of-the-art preparation techniques (Nano-squeegee) to ensure the optimal contact between the TMDs. The Strong ILE emission is observed with the emission energy around 1.35 eV at room temperature and resolve this emission into two distinct peaks (ILE1 and ILE2) separated by 24 meV at zero field at 5 K. Furthermore, we demonstrate that the two emission peaks have *opposite*circular polarizations with up to +20% for the ILE1 and -40% for ILE2 when excited by circularly polarized light. A*b initio* calculations provide an explanation of this unique and potentially useful property and indicate that it is a result of the indirect character of *both* electronictransitions. These peaks are *doubleindirect* excitons. *i.e.*indirect in both real and reciprocal space, split by relativistic effects.

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.

9:20am **2D+EM+MI+MN+NS+QS-TuM-5 Integrating 2D Magnet 1T-$MnSe_2$ with Topological Insulator Bi_2Se_3***, **Tiancong Zhu**,* The Ohio State University*; D O'Hara,* University of California, Riverside*; J Repicky, S Yu, M Zhu, B Noesges, T Liu, M Brenner, L Brillson, J Hwang, F Yang, J Gupta, R Kawakami,* The Ohio State University

Integrating two-dimensional(2D) magnet with topological insulator is an exciting topic. Other than the possible proximity induced magnetic ordering inside topological insulator, the 2D magnet/ topological insulator heterostructure can also lead to more efficient spin orbit torque switching, or the formation of magnetic skyrmions. The recent discovery of room temperature ferromagnetic ordering in 2D material MnSe and VSe further brings more potential in such heterostructure systems. In this talk, we report the synthesis and characterization of 2D magnet 1T-MnSe on topological insulator Bi Se . Monolayer of MnSe is grown on Bi Se with molecular beam epitaxy, and subsequently characterized with various techniques, including X-ray diffractometry (XRD), X-ray photoemission spectroscopy (XPS) and scanning tunneling microscopy (STM). STM measurement reveals the co-existence of monolayer a-MnSe(111) and 1T-$MnSe_2$ on Bi_2Se_3 surface. By performing spin-polarized STM measurement with Cr tip, we observed directly the magnetic signal from 1T-$MnSe_2$ on Bi_2Se_3. The growth of 1T-$MnSe_2$ on Bi_2Se_3 further leads to the MBE synthesis of magnetic topological insulator Bi_2MnSe_4, which also shows ferromagnetism down to the monolayer limit. The structural and magnetic characterization of the material will also be discussed in this talk.

9:40am **2D+EM+MI+MN+NS+QS-TuM-6 Effect of Exchange-correlation Functional and Structural Constraints on the Transition Temperature of Two- Dimensional Ferroelectrics***, **Shiva P. Poudel**, J Villanova, B Miller, A Pandit, S Barraza-Lopez,* University of Arkansas, Fayetteville

In this presentation, I will discuss two inconsistent models for obtaining the transition temperature (T_c) of two-dimensional (2D) ferroelectrics. It will be shown that the inconsistency arises from the choice of exchange-correlation functional and structural constraints [1-4] by obtaining T_c for a SnSe monolayer with PBE and vdW exchange-correlation functional, and with increased constraints. It has been found that vdW functional gives a larger T_c in comparison with PBE functional. Also, the increasing constraint raises T_c as well. Afterward, a complete analysis of the converged unit cell with seven different exchange-correlation functional will be provided. These results represent the most comprehensive theoretical benchmarks for these intriguing 2D ferroelectric materials.

This work was funded by an Early Career Grant from the DOE (Grant No. DE-SC0016139). Calculations were performed on Cori at the National Energy Research Scientific Computing Center (NERSC), a U.S. Department of Energy Office of Science User Facility operated under Contract No. DE-

AC02-05CH11231 and Arkansas High-Performance Computing Center's *trestles*, which is funded through the multiple National Science Foundation grants and the Arkansas Economic Development Commission.

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1. M. Mehboudi et al., Nano Lett. **16**, 1704 (2016).

2. M. Mehboudi, et al., Phys. Rev. Lett. **117**, 246802 (2016).

3. S. Barraza-Lopez, et al., PRB **97**, 024110 (2018).

4. R. Fei, et al., Phys. Rev. Lett. **117**, 097601 (2016).

11:00am **2D+EM+MI+MN+NS+QS-TuM-10 Sign-change Pairing Symmetry in Single Layer FeSe/SrTiO₃ Film***, **Huimin Zhang,*** West Virginia University*; Z Ge, M Weinert,* University of Wisconsin*; L Li,* West Virginia University

Single layer FeSe film epitaxially grown on $SrTiO_3$(001) substrate has drawn much interest for its novel interfacial effects, which have led to the highest superconducting temperature (T_C) to date amongst all Fe-based superconductors. While several paring states, such as sign-persevering s_{++}-wave, sign-changing nodeless *d*-wave and $s_{\pm}$-wave have been suggested, the pairing symmetry remains to be experimentally validated. Here we investigate the intrinsic impurity-induced in-gap bound states and quasiparticle interference (QPI) patterns in single layer FeSe/$SrTiO_3$ by scanning tunneling microscopy/spectroscopy. We observed bound states induced by nonmagnetic impurities, which strongly suggests a sign-changing order parameter. Through detailed analysis of the phase-sensitive QPI patterns, we further confirm that the order parameter indeed changes sign within the electron pockets. This identification of a sign change pairing symmetry in single layer FeSe/$SrTiO_3$ presents a critical step towards the understanding of its high T_c superconductivity.

11:20am **2D+EM+MI+MN+NS+QS-TuM-11 High Temperature Superconductivity in Epitaxial Single Layer $FeTe_{1-x}Se_x$/STO(001)***, **Qiang Zou**, Z Ge, C Yan, H Zhang, L Li,* West Virginia University

Single crystal FeTe exhibits a distinct long-range bicollinear antiferromagnetic order that can be suppressed by alloying with Se, where superconductivity emerges at a critical Se concentration of 0.3 with a T_C of 10 K. In this work, we show that this phase transition can be further modulated by reducing the thickness of $FeTe_{1-x}Se_x$, downto the single atomic layer limit. High quality single layer $FeTe_{1-x}Se_x$ films are grown on $SrTiO_3$(001) substrate by molecular beam epitaxy and characterized by scanning tunneling microscopy/spectroscopy and angle-resolved photoemission spectroscopy. We find the electronic properties are strongly dependent on the Se content. For x < 0.1, hole-like bands cross the Fermi level and form a hole-pocket at the Γ point with no states observed around the M point, indicating no superconductivity. With increasing Se content, the top of the valence bands moves away from the Fermi level, accompanied by a decrease in effective mass at the Γ point. For x > 0.1, the hole pocket at Γ point moves below the Fermi level, and an electron-pocket emerges at M point where a superconducting gap opens with a T_C of ~50 K. These findings and their implications for the emergence and stabilization of superconductivity in Fe-based superconductors at reduced dimensions will be presented at the meeting.

11:40am **2D+EM+MI+MN+NS+QS-TuM-12 The Observation of Majorana Zero Mode and Conductance Plateau in an Iron-based Superconductor***, **Hong-Jun Gao**,* Institute of Physics, Chinese Academy of Sciences, China **INVITED**

Majorana zero-modes (MZMs) are spatially-localized zero-energy fractional quasiparticles with non-Abelian braiding statistics that hold great promise for topological quantum computing. Recently, by using scanning tunneling microscopy/spectroscopy (STM/STS), a new breakthrough of Majorana zero mode (MZM) was achieved in a single material platform of high-T_c iron-based superconductors, $FeTe_{0.55}Se_{0.45}$, which combined advantages of simple material, high- T_c, and large ratio of Δ/E_F [1]. A detail STM/STS study of a $FeTe_{0.55}Se_{0.45}$ single crystal, also revealed the mechanism of two distinct classes of vortices present in this system, which directly tied with the presence or absence of zero-bias peak [2]. To further investigated the MZM, it is still needed to find a "smoking-gun" type of evidence for the existence of MZM, and a quantized conductance plateau is widely believed to be one of them. Here we report an observation of the Majorana conductance plateau in vortices on the iron superconductor $FeTe_{0.55}Se_{0.45}$ surface by using STM/STS [3]. We found that both extrinsic instrumental convoluted broadening and intrinsic quasiparticle poisoning can reduce the conductance plateau value. When extrinsic instrumental broadening is removed by deconvolution, the plateau is found to nearly reach a $2e^2/h$ quantized value. The direct observation of a conductance plateau on a single zero-mode in a vortex strongly supports the existence and protection of MZMs in this iron-based superconductor, which can serve as a single-material platform for Majorana braiding at relatively high temperature.

* In collaboration with, D.F. Wang[1,2], L.Y. Kong[1,2], P. Fan[1,2], H. Chen[1], S.Y. Zhu[1,2], W.Y. Liu[1,2], L. Cao[1,2], Y.J. Sun[1,2], S.X. Du[1,2,3], J. Schneeloch[4], R.D. Zhong[4], G.D. Gu[4], Liang Fu[5], Hong Ding[1,2,3].

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Electronic Materials and Photonics Division
Room A214 - Session EM+2D+AP+NS+PS-TuM

New Devices and Materials for Electronics and Photonics

Moderators: Sean W. King, Intel Corporation, Michelle M. Paquette, University of Missouri-Kansas City

8:00am **EM+2D+AP+NS+PS-TuM-1 Performance Modeling and Design for Spintronic Logic and Memory Devices***, **Azad Naeemi,*** Georgia Institute of Technology **INVITED**

As scaling conventional logic and memory devices becomes more and more challenging, there is a global search for novel materials and devices that can augment mainstream technologies used for data storage and processing. To this end, spintronic materials and devices are promising candidates as they provide dense non-volatile storing elements that enable novel computing paradigms such as in memory-computing and neural networks.

This talk will present physical models for various read and write spintronic mechanisms and quantifies the potential performances of Boolean circuits based on various spintronic logic devices. It will be shown that without major breakthroughs such circuits will not be able to compete with their CMOS counterparts. However, novel circuit paradigms that take advantage of the physics of these devices can potentially provide significant benefits. For example, cellular neural networks based on spintronic devices are projected to perform better compared to their analog CMOS implementation.

While spin-transfer-torque random access memory (STT-RAM) is becoming commercially available, it suffers from relatively large switching currents that limits its density and causes reliability challenges. Novel read and write mechanisms such as spin-orbit torque or magneto-electric effects can potentially address or partially mitigate some of these challenges. In this talk, the array-level potential performance of various magnetic memory devices will be quantified and benchmarked.

8:40am **EM+2D+AP+NS+PS-TuM-3 High Yield, Low Variability HfO_2 1T1R Cells Fabricated in 65nm CMOS***, **Jubin Hazra**, M Liehr, K Beckmann, N Cady,* SUNY Polytechnic Institute

Hafnium Oxide (HfO_2) based Resistive Random Access Memory (ReRAM) devices are promising candidates for non-volatile memory, having a wide variety of applications in neuromorphic computing, artificial intelligence and future memory solutions. Stochastic conductive filament (CF) generation and rupture processes, however, contribute to high variability resistive switching in these devices. In order to address this issue, an extensive characterization of HfO_2 1 transistor 1 RRAM (1T1R) cells was performed to investigate switching yield and cell-to cell variability. 1T1R devices were integrated into a 300mm wafer platform utilizing the IBM 65nm 10LPe process technology, in which the memristor device stack is implemented between the M1 and M2 metallization layers, using a custom designed FEOL compatible process flow. The ReRAM device stack is comprised of a TiN bottom electrode followed by conformal deposition of the HfO_2 switching layer, Ti oxygen scavenging layer and TiN top electrode.

The HfO_2 switching layer was deposited using an atomic layer deposition (ALD) process with an organic precursor. For statistical significance, the performance of 50 different 1T1R cells was compared for cell-to-cell variability in operating voltage and resistance in the on and off state. An impressive 100% switching yield and low cell-to-cell switching variability were observed for these devices. 1T1R cells were also investigated for long term endurance and high temperature retention, exhibiting excellent endurance of up to 1 billion switching cycles with an average R_{off}/R_{on} ratio of 10:1. As compared to 1T1R cells that we have fabricated with alternative ALD precursors/methods, these devices show superior yield and performance. We are currently performing compositional and structural comparisons between these sets of devices, to elucidate the impact of ALD precursor choice and processing methods on yield and electrical performance.

9:00am **EM+2D+AP+NS+PS-TuM-4 Heat Transfer Proximity Effects in Resistive Memory Crossbar Arrays***, **Marius Orlowski**, M Al-Mamun,* Virginia Tech

Evidence for thermal cross talk in resistive RAM memory arrays is presented. Frequent switching of a resistive memory cell ($Cu/TaO_x/Pt$) may lead to a considerable local accumulation of Joules heat. The heat generated in a stressed device spreads via common electrode lines to the neighboring cells impacting their switching behavior. As a probe into degraded performance of the neighbor cells we choose the cell itself set into the on-state under specific conditions. The cell is set at a critical compliance current I_{cc} that allows repeated switching for no more than ~15 cycles. After the maximum number of cycles the on-state becomes volatile. For a lower I_{cc}, the cell produces a volatile on-state, and for higher I_{cc} the cell switches for hundred of times with a stable on-state. We find that the cells in close proximity of the heated device display various degrees of degradation indicated by a reduced number of cycles of the probed cell. The 1st neighbor cell experiences the greatest, and the 4th neighbor cell the smallest degradation. This indicates the spread of the heat from the heated device to its neighbors. After a sufficient cooling off period (10 minutes or longer), all the neighboring cells and the heated device display again the maximum number of cycles i.e. 15, when set under the critical compliance current and reset, repeatedly. Also cells that don't share any of the common electrode metal lines with the heated source cell, may degrade provided that the intermediate cells are set to on-state, thus enabling a continuous thermal conduction path between the heated cell and the probed cell. The heat dissipation from the heated device is slower for narrow and thin metal electrode lines than for wide and thick metal lines. However, in case of wide and thick metal lines more distant neighbor cells are affected by the parasitic cell-to-cell heat transfer.

We have performed the characterization o the neighboring cells along the Cu and Pt electrode lines. We find that the performance degradation of the neighboring cells along the Cu line is significantly stronger than along the Pt metal line. This observation is consistent with the much better heat conductivity of Cu lines (385W/(mK) and 150nm thick) than the Pt (72W/(mK) and 50nm thick) lines, but is at odds with the assumption of the standard electro-chemical metallization model postulating a conical shape of the Cu filament with a broad base of the cone at the Pt electrode and a tip at the Cu electrode. We discuss the extant controversial experimental evidence and models for the filament's shape and propose an hour-glass shape for the filament reconciling the extant findings and our thermal results.

9:20am **EM+2D+AP+NS+PS-TuM-5 High Performance Memristive Action in Methylammonium Bismuth Iodide([MA]3Bi2I9) Films***, P Cheng,* Vanderbilt University*; G Luo,* Washington University in St. Louis*; Z Gao,* University of Central Florida*; A Thind, R Mishra,* Washington University in St. Louis*;* ***Parag Banerjee,*** University of Central Florida

We demonstrate high performance (ON/OFF ~ $2.4x10^5$) resistive switching in methylammonium bismuth iodide ($(CH_3NH_3)_3Bi_2I_9$ or, MBI) thin films.[1] MBI has a post-perovskite structure and consists of 2D layers of face-shared BiI_6 octahedra. This talk focuses on the structure, composition and associated defect chemistry that is critical for memristive behavior in MBI films.

Memristors are formed by contacting MBI films with aluminum electrodes. The switching for a 200 nm film is observed at voltages ~ 0.5 V. High frequency performance of these memristors shows a peak ON/OFF ratio $2.4x10^5$at 50 KHz. The ON state retention is maintained at 50C for > 10^6 seconds. Stable room temperature endurance is noted for up to 1000 cycles. Energy dispersive x-ray spectroscopy on planar memristor devices show that, postswitching, a detectable change in the I- concentration is observed closer to the anode side. Density-functional theory (DFT) calculations show low activation barrier for iodine migration in agreement with the experimental results. The DFT calculations also provide insights about the migration pathway and strategies to control this behavior.

From a synthesis perspective, MBI films can be deposited using solution as well as low temperature (< 200C), atmospheric CVD technique.[2] The compounds are air stable. This family of ternary compounds offers a large compositional and structural tunability; unlike binary metal oxides commonly used for memristors. As opposed to recent 2D MoS_2 based planar, tunneling RAM devices[3], the vertical stack of the 2-terminal memristor bodes well for scalability. Thus, we propose that hybrid organic-inorganic thin films may offer strategic materials and design advantages together with seamless process integration into current Si-based devices.

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9:40am **EM+2D+AP+NS+PS-TuM-6 Mechanism of Chalcogen Passivation of GaAs Surfaces***, **Takayuki Suga**, S Goto,* UEC-Tokyo, Japan*; A Ohtake,* NIMS, Japan*; J Nakamura,* UEC-Tokyo, Japan

GaAs surfaces are stabilized by surface treatments with Se or S through the reduction of the dangling bond density [1,2]. It has long been thought that the Se- or S-treated GaAs(111)B-(1x1) surface has a simple structure; the outermost As atoms of the ideal (111)B surface are completely replaced by Se or S atoms, the Se- or S-terminated model [3]. In general, the structural stability of compound semiconductor surfaces can be explained in terms of the so-called electron-counting rule (ECR) [4]. The Se- or S-terminated model, however does not satisfy ECR. Recently, the atomic structure of the Se-treated GaAs(111)B surface has been revisited [5] and another structure model has been proposed, where the Se atoms substitute 3/4 of the topmost surface As atoms in a (2x2) unit [6]. This mixed Se/As-terminated model satisfies ECR, being electronically stable [6]. We have depicted phase diagrams of Se- or S- treated GaAs(111)B surface at 0K as functions of the chemical potentials of Se ($\Delta\mu_{Se(S)}$) and As ($\Delta\mu_{As}$). The (2x2) As-trimer and the mixed Se(S)/As-terminated surfaces appear under Se poor condition. It is noted that the Se- or S-terminated surface also becomes stable as $\Delta\mu_{Se}$ or $\Delta\mu_{S}$ increases, respectively, even though these surfaces are not qualified for ECR.

The Se(S)-treated GaAs(111)B surface is prepared experimentally by molecular beam epitaxy under a finite temperature and a gas pressure. Therefore, it is necessary to consider the free energy of a molecule in vapor phase. In this study, we investigate the stabilization of the Se- or S-treated GaAs(111)B surface structures by considering the beam equivalent pressure of As and Se(S) in a growth temperature using the first-principles calculations within the density functional theory. The chemical potentials of molecules are derived from the partition functions for the translation, the rotation, and the vibrational motions.

In the phase diagram for the actual experiment condition, T=800K, the mixed Se/As terminated surface appears in the Se pressure of 10^{-15}-10^{-5} Torr, being consistent with the recent experiment [5]. Surprisingly, the Se-terminated surface also becomes stable as the Se pressure increases. We will discuss the stabilization mechanism of the chalcogen-treated GaAs surfaces.

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11:00am **EM+2D+AP+NS+PS-TuM-10 Combining 2D and 1D Atomic Scale Tailored Nanowire Surfaces for Novel Electronics and Photonics*, Anders Mikkelsen,*** Lund University, Sweden **INVITED**

The III-V nanowire (NW) technology platform has reached a level of advancement that allows atomic scale control of crystal structure and surface morphology as well as flexible device integration. In particular, controlled axial stacking of Wurtzite (Wz) and Zincblende (Zb) crystal phases is uniquely possible in the NWs. We explore how this can be used to affect electronic, optical and surface chemistry with atomic scale precision opening up for 1D, 2D and 3D structures with designed local properties.

We have previously demonstrated atomically resolved Scanning Tunneling Microscopy/Spectroscopy (STM/S) on a wide variety of these III-V NWs and on operational NW devices[1-4]. We now use these methods for studying atomic scale crystal phase changes, the impact on local electronic properties and demonstrating full atomic resolution STM during device operation[5-7]. We explore the surface alloying of Sb into GaAs NWs with controlled axial stacking of Wz and Zb crystal phases[5] demonstrating a simple processing-free route to 1D and 2D compositional control at the monolayer level. Further we show how Bi can form unique 1D and 2D structures in particular on the unique Wz GaAs NW segments. Using 5K STM/S we measure local density of states of Zb crystal segments in Wz InAs NWs down to the smallest possible atomic scale crystal lattice change [6], which is effectively a small 2D material segment in a 1D structure. We find that the general Zb electronic structure is preserved locally in even the smallest segments and signatures of confined states in them.

Characterization to the atomic scale during electrical and optical operation is necesarry to understand and develop the functionality of structures as discussed above. We demonstrate a novel device platform allowing STM/S with atomic scale resolution across a III-V NW device simultaneously with full electrical operation and high temperature processing in reactive gases[7].Using 5-15 femtosecond laser pulses combined with PhotoEmission Electron Microscopy (PEEM) we explore local dynamic response of carriers in the 1D Wz and Zb crystal phases down to a few femtoseconds temporally and a few tens of nanometer spatially[8].

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11:40am **EM+2D+AP+NS+PS-TuM-12 Nanoflower Decorated GaN and AlGaN/GaN based Catalyst-free CO Sensors*, Monu Mishra,*** *G Gupta,* National Physical Laboratory, India

III-Nitride semiconductors owing unique material properties have proven their potential in the detection of light, chemical, biomolecules and toxic/explosive gases. Despite of numerous advantages *viz.* biocompatibility, high temperature/frequency tolerance and harsh/adverse environmental condition sustainability, the use of expensive catalysts (e.g. platinum) and higher operation temperature (>250°C) for gas sensing has plagued the development of GaN based cost-effective sensing technology. Upto the best of our knowledge, literature lacks any scientific report on the development of catalyst-free CO sensors operating at room-temperature using GaN or AlGaN/GaN structures indicating the necessity of dedicated scientific attention in this area. Therefore, we report the fabrication of nanoflowers-decorated GaN and AlGaN/GaN heterostructure based catalyst-free CO sensors operating at lower (including room) temperature. Planar as well as nanostructured GaN & AlGaN/GaN thin films were employed for sensors fabrication which exhibited significant CO sensing associated with its superior surface and interface properties. For in-depth understanding, the obtained results were thoroughly analyzed and correlated to investigate the underlying science/phenomenon which revealed that CO sensing on GaN (and AlGaN/GaN) is governed by the chemical nature of ambient-oxidation induced amorphous oxide (O_2^-, O^{2-} orOH^- species) layer grown on the surface and acting as a donor/acceptor state. Besides, electron accumulation at AlGaN/GaN interface influenced the critical parameters like schottky barrier height, ideality factor etc. perturbed the effective carrier transport and ultimately the device performance. The study demonstrate that development of catalyst-free room temperature operating GaN based CO sensors is feasible using nanostructured surfaces, though further research is required for optimization of device performance.

12:00pm **EM+2D+AP+NS+PS-TuM-13 Surface Transfer Doping of Diamond by Complex Metal Oxides for Power Electronics: A Combined Experimental and Simulation Study*, Vihar Georgiev,*** *D Moran, J McGhee,* University of Glasgow, UK

Diamond has unique properties that make it an attractive wide band-gap material to produce future high-performance electronic devices. With a wide band-gap of 5.5eV, a thermal conductivity 5 times greater than 4H-SiC, a high breakdown field and high hole and electron carrier velocities, diamond is a clear stand out candidate for high frequency and high power devices. However, the lack of a suitable doping mechanism has hindered the application of diamond in electronic devices. Conventional substitutional doping techniques are limited as it is difficult to substitute atoms into the diamond crystal lattice.

Surface Transfer Doping (STD) gives the use of diamond for such applications more promise. For STD to occur there are typically two prerequisites: hydrogen terminated diamond (H-diamond) and an electron accepting material in intimate contact with the H-diamond surface. The hydrogen termination gives the diamond a negative electron affinity which facilitates the transfer of electrons from the diamond to the electron-accepting material, creating a shallow, quasi two-dimensional hole gas (2DHG) in the diamond. This doping process traditionally relies upon interfacial electron transfer between the diamond valence band and favourable energy states provided by atmospheric molecules dissolved in a water layer naturally adsorbed on the diamond surface. However, the stability of this atmospheric layer, upon which the transfer doping process relies, has been a significant limiting factor in the production of high-power handling and robust operation devices.

One of the materials that can improve the performance and stability of STD in diamond are the metal oxides such as MoO_3 which acts as an alternative electron acceptor medium on the H-diamond surface. In order to validate and understand the physical and the chemical process in such STD, in this work we have combined experimental and simulation studies. The electrical characterisation is done by high temperature Hall measurements. Those experimental results are compared to numerical simulation based on the first principle methods such as Density Functional Theory. Comparing the simulation and experimental results revealed that the electrons are transferred from the diamond to the metal oxides, leading to formation of a sub-surface 2DHG in the diamond. Due to this transfer of electrons to the oxide the hole carrier concentration increases in comparison to the air-exposed H-diamond. Our work shows the potential to improve the stability and performance of hydrogen-terminated diamond electronics devices through incorporation of high electron affinity transition metal oxides.

Plasma Science and Technology Division
Room B131 - Session PS+EM-TuM

Advanced FEOL

Moderators: Keren Kanarik, Lam Research Corporation, Alok Ranjan, TEL Technology Center, America, LLC

8:00am **PS+EM-TuM-1 Investigation on Plasma Etch Technology Enabling Si/SiGe MOSFET Process Integration*, Yohei Ishii,*** Hitachi High Technologies America Inc.*; Y Lee, W Wu,* Taiwan Semiconductor Research Institute, Taiwan, Republic of China*; R Sugano,* Hitachi, Ltd., Japan*; K Maeda,* Hitachi High Technologies America Inc.*; H Ishimura,* Hitachi High-Technologies Taiwan Corp., Taiwan, Republic of China*; M Miura,* Hitachi High Technologies, Japan **INVITED**

Many challenges have emerged due to down-scaling of device structure in order to follow Moore's law. By modifying the transistor structure from planar to Fin-type Field Effect transistors (FinFETs), transistor electro-statics were improved, which led to overcoming short-channel effects. However, the change is no longer sufficient, and the semiconductor industry faces difficulty to further improve the transistor performance. One of the promising candidates for the improvement in sub-10nm process is to utilize Silicon/Silicon-germanium (Si/SiGe) dual channel FinFETs (Si in n-FETs and SiGe in p-FETs). In this case, simultaneous etching of Si and SiGe is required [1]. However, etch rate of SiGe is greater than Si for halogen chemistries commonly used in Si etch. Therefore, it is required to develop selective Si etch over SiGe for etch rate control between these two materials.

In order to maximize electrical performance of SiGe, modifying the SiGe surface composition into Si-rich surface at SiGe/gate-oxide interface is critical to reduce interface state density due to the impact on sub-threshold characteristics [2]. Traditional methods to produce Si-rich surface are epitaxial growth of Si cap over SiGe fin [3] and GeOx-scavenging process [4]. However, thermal budgets of these methods are relatively high, and there are concerns of strain relaxation in SiGe channel and Ge diffusion into Si substrate, both of which deteriorate the FET characteristics. Hence, a low-temperature process to produce Si-rich surface is required.

In this presentation, we will present two phenomena; one is Si-SiGe selective etch control, and the other is SiGe surface composition modification of SiGe into Si-rich surface by low temperature plasma. We will first present a plasma process, which etches Si selective to SiGe for Si-SiGe etching control, and will discuss the etching mechanism of the selective etching. We will then present the composition modification into Si-rich surface by utilizing Si segregation from the low temperature plasma process. This plasma etch technique can solve the etch rate control and surface composition challenges, which can be a promising scheme for realizing well-controlled SiGe finFETs with improved characteristics.

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8:40am **PS+EM-TuM-3 Etching of Sub-10 nm Half-pitch High Chi Block Copolymers for Directed Self-Assembly (DSA) Application***, **Maria Gabriela Gusmão Cacho**, P Pimenta-Barros, K Benotmane, A Gharbi, M Argoud,* CEA-LETI, France*; C Navarro,* Arkema France, France*; K Sakavuyi,* Brewer Science Inc.*; R Tiron, N Possémé, S Barnola,* CEA-LETI, France

As the semiconductor industry approaches the smaller technologic nodes such as the sub-10 nm, conventional lithography technologies have reached their limit. Among the different approaches investigated to continue pattern scaling, Directed Self-Assembly (DSA) of Block Copolymers (BCP) is one of the most promising due to its simplicity, low manufacturing cost and capability to design high density cylindrical or line/space patterns. For the last few years, PS-*b*-PMMA has been the most used BCP for this application. However, since the minimum feature size for the PS-*b*-PMMA system is limited to ~13 nm due to its low interaction parameter (also known as “chi”), new systems have been developed to achieve higher resolution by improving its microphase separation strength, thus obtaining the so called “high chi” BCPs.

In this paper, the high chi BCP system investigated is a modified PS-*b*-PMMA that presents a pitch of 18 nm, which will be referred to as “L18”. One critical step for its integration is the PMMA removal selectively to the PS. The results obtained with both dry and wet etching of the L18 BCP are presented, highlighting the challenges encountered due to its smaller dimensions.

A wet PMMA removal process based on UV exposure followed by IPA rinse will be presented. An Ar/O_2 dry etch step for the brush layer opening was developed and the transfer of the line/space pattern into the SiO_2 and Si underlayers was demonstrated for the L18 BCP. However, this wet development is expected to cause pattern collapse when the BCP will be guided by chemoepitaxy due to capillary forces.

Therefore a complete PMMA removal by dry etching alone was also investigated. Different etching chemistries based on $CH_3F/Ar/SO_2$, CH_4/N_2 or cyclic CO + CO/H_2 were applied to the modified PS-*b*-PMMA BCPs with a 30 nm pitch and with an 18nm pitch (L18). For the 30 nm-pitch BCP, all three plasma chemistries allow the complete PMMA and brush layer removal by dry etching and the subsequent pattern transfer into the SiO_2 layer. In contrary, for the L18 BCP, the $CH_3F/Ar/SO_2$ plasma does not present enough PS budget for pattern transfer due to its low selectivity and the small thickness of the BCP. For the more passivating chemistries such as CH_4/N_2 and cyclic CO + CO/H_2, which have higher selectivity, we observe the formation of bridges that prevent complete pattern transfer. We used *ex-situ* X-ray Photoelectron Spectroscopy (XPS) to investigate the origin of these bridges and to understand the etching mechanisms present.

9:00am **PS+EM-TuM-4 Mechanism of Highly Selective SiCN Etchings Using NF_3/Ar-based Gases***, **Miyako Matsui**,* Hitachi Ltd., Japan*; K Kuwahara,* Hitachi High-Technologies Corp., Japan

Highly selective etchings over various other materials are increasingly required to achieve self-aligned processes, which provide higher density devices without shrinkage of the pattern dimensions in three-dimensional devices, such as fin-based field-effect transistors. In a self-aligned process, SiCN etching is required to achieve high selectivity to both SiO_2 and Si_3N_4. However, it had been difficult to achieve high selectivities to both SiO_2 and Si_3N_4 using fluorocarbon gas chemistries. For example, selectivity to SiO_2 increased using a hydrofluorocarbon plasma, while selectivity to Si_3N_4 decreased. So, it is important to investigate gas chemistries to simultaneously control selectivities to various materials.

In this study, mechanisms for highly selective SiCN etchings with microwave ECR plasma using NF_3/Ar-based gases were investigated over various materials. The rate of SiCN etching using NF_3/Ar plasma was higher than that of other materials, which were TiN, poly-Si, SiO_2, and Si_3N_4. The SiCN was etched with NF_3/Ar plasma, which formed SiF_x and FCN. On the other hand, other materials were etched with low rates. To achieve higher selectivities, the effects of adding gases to NF_3/Ar plasma on various materials to inhibit etching were analyzed by X-ray photoelectron spectroscopy (XPS).

Firstly, a highly selective SiCN etching over poly-Si was achieved by adding O_2 to NF_3/Ar plasma. This was because poly-Si etching was inhibited by the formation of a 1.0 nm-thick oxidized layer, which protected the poly-Si surface from the etching reaction with F radicals. The SiCN etch rate also decreased when the poly-Si etching was stopped. However, C atoms contained in the SiCN layer reacted with O radicals and controlled oxidization of the SiCN surface.

Next, highly selective SiCN etchings over SiO_2 and Si_3N_4 were achieved by using a NF_3/Ar-based plasma by which deposited layers were formed on the surfaces. The deposited layers formed on the SiO_2 and Si_3N_4 protected the surfaces from being etched by reacting with F radicals. On the other hand, the deposited layer was thought to be more difficult to be formed on the SiCN.

Lastly, highly selective etching over TiN was achieved by using H_2-added plasma. XPS result showed that a thin protective layer containing TiF_x and ammonium fluoride, which is decomposed over 673K, had been formed on the TiN surface. The protective layer formed on the TiN surface was very effective at protecting the TiN from being etched by F radicals.

In conclusion, we achieved extremely highly selective SiCN etchings over various materials by forming protective layers, which were formed on non-etched materials by adding gases to NF_3/Ar plasma.

9:20am **PS+EM-TuM-5 Impact of Plasma Process on Source/Drain Epitaxy Film***, **Yun Han**, B Messer, M Sapel, H Kim, Y Shi, M Wang, Y Trickett, K Maekawa,* TEL Technology Center, America, LLC*; K Taniguchi, S Morikita,* Tokyo Electron Miyagi Ltd., Japan*; A Metz, P Biolsi,* TEL Technology Center, America, LLC

Middle-of-Line (MOL) contact open by plasma etching is a very critical step in logic IC fabrication. Source/Drain Epitaxy (S/D Epi) film as a key element in device transistors controls device performance in various aspects. S/D Epi film damage induced by plasma etch processes have been one of the challenges in MOL integration. Epi film damage includes surface roughening and oxidation, crystal structure relaxation and elemental doping, all of which could lead to uncontrolled variation and degradation in electrical performance of the devices. In this paper, SiGe (known pMOS S/D material) film damage post varying CCP plasma conditions have been studied by utilizing different characterization techniques including X-ray photoelectron spectroscopy (XPS), Transmission Electron Microscope (TEM) / Energy-dispersive X-ray spectroscopy (EDS), Rutherford backscattering spectrometry (RBS) and Secondary ion mass spectroscopy (SIMS). Various CCP plasma conditions include changes in gas chemistries (N/H/O/C/F/Ar), plasma source/bias power and chamber configurations. Electrical response on short loop device wafers have been collected and correlated with observed physical/chemical changes in S/D Epi film post plasma processes. We also performed molecular dynamics, quantum chemistry and chamber scale simulation to understand the fundamental chemical behavior and characterize the surface/chemical properties between provided plasma and SiGe film at various ion energy and ion/radical flux in an atomic/molecular level. The study provides a comprehensive understanding in plasma damage to S/D Epi film and a fundamental guideline in optimizing plasma processes to achieve ideal contact open etch with minimal damage on source/drain Epi film.

9:40am **PS+EM-TuM-6 CCP Dry Clean Process Development Using Quadrupole Mass Spectrometer and Optical Emission Spectroscopy***, **Harutyun Melikyan**, A Martinez, S Pandey, M Koltonski, G Sandhu,* Micron Technology

Dual frequency capacitive coupled plasmas provide flexible control of ion energy distributions, enabling high selectivity for etching of different materials, and flexibility to develop more efficient dry clean processes for higher productivity. It is common for each patterned wafer etch to have pre and post dry clean steps, with and without wafer, respectively. The primary focus of dry etch engineers is to design high etch rate processes, with minimized process time, and without changing the critical dimensions. Additionally, significant gains can be achieved by optimizing the dry clean recipes because they contribute significantly to the raw process time. In some cases, it can take a long time to achieve proper pre and post conditioning of the chamber.

In this work, we show that real-time monitoring techniques can be used to provide insight into the etch process byproducts, enabling intelligent development of the dry clean recipes. Integrating quadrupole mass spectrometry and optical emission spectroscopy with the capacitive coupled plasma reactor, and monitoring in parallel, we were able to identify 99% of the patterned wafer etch byproduct species with high confidence. Knowing the etch byproducts provides a clear path to an optimized dry clean process. We were then able to develop the dry clean recipe with appropriate precursor gases to increase volatile byproducts significantly (e.g. SiF4 at 33%) and minimize non-volatile byproducts (e.g. ammonium salts at <1%), resulting in a 70% reduction of dry clean process time.

11:00am **PS+EM-TuM-10 Surface Reaction of Atomic Hydrogen with SiGe Surface Compared with Si Through Ab-initio Calculations***, **Ryoko Sugano**,* Hitachi, Ltd., Japan*; Y Ishii, K Maeda,* Hitachi High Technologies America Inc.*; M Miura, K Kuwahara,* Hitachi High Technologies, Japan

Simultaneous etching of Si and SiGe is an indispensable process for high throughput in the fabrication of Si/SiGe dual-channel FinFETs. SiGe etch rate is higher than Si etch rate by typical halogen chemistries used for Si etching [1]. Therefore, to control the etch rate between Si and SiGe, it is necessary to develop the chemistry that gives a higher Si etch rate than SiGe etch rate. Recently Ishii et al. have reported that hydrogen plasma selectively etched Si over SiGe, showing the selective Si removal over Ge [2]. In spite of selective Si etching over Ge, the Si-rich surface was observed after the hydrogen plasma exposure. They have attributed the Si-rich surface to hydrogen-induced Si surface segregation [2].

To understand the mechanism of the experimental phenomena on SiGe film described above, we performed ab-initio calculations that combined geometry optimizations and Nudged Elastic Band calculations. In the hydrogen-terminated SiGe surface system, we assumed the reacted states of SiGe were single dimer, in which three hydrogen atoms adsorbed on one of the dimer atoms (SiH3, GeH3) and a single hydrogen atom adsorbed on another of the dimer atoms. We found that the formation with SiH3 was energetically stable and was easy to desorb with a lower activation energy than that with GeH3. We considered that the selective Si removal over Ge was caused by both the selective formation and selective desorption of SiH3. We also calculated the formation energy of the SiGe surface immediately after selective Si removal, which originated from dimer breaking. It was found that the site exchange between the Ge atom in the first layer and the Si atom in the second layer was energetically favorable when another dimer atom left on the surface was terminated with a hydrogen atom. In conclusion, we confirmed experimental results of both selective Si etching over SiGe and Si surface segregation under the condition of hydrogen plasma by performing ab-initio calculations.

[1] G. S. Oehrlein, et al., Appl. Phys. Lett. 58, 2252 (1991).

[2] Y. Ishii et al., Jpn. J. Appl. Phys. 57, 06JC04 (2018).

11:20am **PS+EM-TuM-11 Nanopantography with Reusable Membrane-based Electrostatic Lens Arrays***, **Ryan Sawadichai**, Y Chen, P Basu, V Donnelly, P Ruchhoeft, D Economou,* University of Houston

Nanopantography is a method for massively parallel writing of nano-sized patterns using an ion beam in combination with a reactive gas. In this process, a broad area, collimated, nearly-monoenergetic ion beam is directed towards an array of micron-scale electrostatic lenses in direct contact with a substrate. By applying an appropriate DC voltage to the lens array with respect to the substrate, the ion beamlet entering each lens converges to a fine spot that can be 100 times smaller than the diameter of each lens. Previously, lenses fabricated directly on the silicon substrate were used to etch 3 nm diameter holes in silicon by exposure to a monoenergetic Ar^+ ion beam and chlorine gas. This work reports on the development of removable and reusable free-standing membrane-based electrostatic lens arrays that are designed to pattern any conducting surface. The lens arrays were fabricated on a silicon wafer coated with PMGI, SU-8, gold, copper, and PMMA. Lens openings were lithographically defined, and an acrylic frame was placed over the array. The lens patterns were etched through the SU-8 and the membrane was released by dissolution of the PMGI layer. The applied voltage used to focus the ion beamlets also served to electrostatically clamp the lens array to a conducting substrate, which was observed as a flattening of the membrane against the substrate surface and an increasing capacitance measured between the lens array and the substrate. An array with lens diameters between 0.8 µm and 1.5 µm and dielectric thickness of 1 µm was used to pattern nanoscale features on a silicon substrate using a 70 eV Ar^+ ion beam and chlorine gas. Ion trajectory simulations were performed to understand the sensitivity of minimum feature size to the variation of lens potential, lens aspect ratio, and lens size. Simulations agreed with the experimentally observed patterns when chromatic and spherical aberrations were considered. With a thinner dielectric and higher lens voltage, it should be possible to print sub 10-nm features in a step and repeat nanopantography process.

Thin Films Division
Room A122-123 - Session TF+EM+MI-TuM

Thin Films for Microelectronics, Photonics, and Optoelectronic Applications

Moderators: John F. Conley, Jr., Oregon State University, Halil Akyildiz, Uludag University, Turkey

8:00am **TF+EM+MI-TuM-1 Monolithic Integration of III-Vs on Si for Electronic and Photonic Applications***, P Staudinger, S Mauthe, N Vico Trivino, M Sousa, C Convertino, Y Baumgartner, P Tiwari, H Schmid, **Kirsten Moselund**,* IBM Research Zurich, Switzerland **INVITED**

For more than half a century researcher have been working on monolithic integration of III-V materials on Si in order to achieve seamless integration of III-V with Si CMOS. Progress has been made in recent years for example on nanowires [1], aspect ratio trapping (ART) [2] and other selective growth techniques suitable for III-V device integration. Here, I will discuss our work on Template-Assisted Selective Epitaxy (TASE) [3], as a novel epitaxial technique where III-V nanostructures are grown within an oxide template.

In this method we first use a combination of lithography and etching to define our structures in Si. These might be vertical or lateral nanowires, or more exotic shapes such as hall-bars, rings and disks. The Si features are covered by an oxide, which is opened locally, and the Si is partially etched exposing a Si nucleation seed within a hollow oxide cavity (template). The template is subsequently filled by metal-organic chemical vapor deposition (MOCVD) grown III-V material. The geometries of the III-V features are lithographically defined by the shape of the hollow template and to a large extent independent of growth conditions.

The versatility of this technique will be shown through several experimentally demonstrated devices, such as InGaAs MOSFETs [4], heterojunction tunnel FETs [5] and monolithically integrated room temperature optically pumped GaAs [6] and InP microdisk lasers [7].

The quality of the TASE-grown material is assessed by high-resolution scanning transmission electron microscopy (HR-STEM). Devices are free from propagating defects and dislocations, but stacking faults are present as expected for selective epitaxy. By controlling the twinning, we were successful in demonstrating pure wurtzite InP micro-substrates for the first time. We also compare lasing performance to that of devices based on defect-free bonded material, which currently represents the state-of-the-art in terms of photonic integration.

This work received funding from H2020 ERC project PLASMIC (Grant No. 678567), SiLAS (Grant No. 735008) and the SNF (Project 200021_156746).

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8:40am **TF+EM+MI-TuM-3 A Scheme for Better Future Technology by developing AlGaN based Highly Responsive Photosensing Devices**, ***Neha Aggarwal***, *S Krishna, L Goswami, G Gupta,* CSIR-National Physical Laboratory, India

All species on Earth are affected by UV radiation, from environment-to-humans, industrial-to-residential, defense-to-technology; a number of current & futuristic applications of detecting UV radiation exist. For fabricating UV photodetectors (PDs), III-Nitrides are promising candidates due to their superior material properties such as wide-direct bandgap, high thermal conductivity, good radiation hardness, etc. Also, III-nitrides are intrinsically blind to the visible region of EM spectrum; thus, do not require expensive optical filters unlike existing Si-based UV PDs. Among nitrides, AlGaN based heterostructures have gained huge interest in optoelectronic applications due to their ability to tune the bandgap by modulating Al concentration which allows them to select the cut-off wavelength depending upon the application. Further, to facilitate the integration of AlGaN based devices with existing Si technology, Si substrates were utilized for growing AlGaN heterostructures. However, large lattice mismatch between AlGaN & Si may restrict the growth of defect-free AlGaN, thus a nucleation layer is needed to avoid cracking due to tensile strain. Incorporation of AlN as interlayer reforms the tensile stress in AlGaN layer directly grown on Si into compressive stress which yields the desired crack-free epitaxial structure. In this work, extensive efforts are employed to grow AlN on Si (111) substrate via PAMBE & successfully accomplished best quality AlN with lowest HRXRD FWHM of 15 arcmin having screw dislocation density of 8.5×10^{8} cm^{-2}. Then, we have performed hetero-epitaxial growth of Al$_x$Ga$_{1-x}$N on AlN buffered Si (111) for x in 0.30-0.45 range & discusses the compositional fluctuations associated with changes in buffer growth parameters. As the buffer growth conditions changes, Al composition varies from 0.30-0.45 & FWHM is reduced from 55.6 to 36.4 arcmin. To realize a highly responsive UV PD, uniformly oriented AlGaN nano-islands are grown aimed to efficiently absorb photons due to increased surface-to-volume ratio. On this, we also implemented interdigitated (ID) electrode configuration to collect higher photo-generated charge carriers. The fabricated AlGaN UV PDs having cut-off wavelength of 284 nm yielded a significant enhancement in responsivity from 36.4 to 140.5 A/W at 2 V bias upon changing electrodes from non-ID to ID. However, the developed UV detection device exhibit high response towards UV with responsivity value of 182 mA/W under 2.5 V bias which is better than the commercially available UV detectors. Conclusively, the highly responsive AlGaN UV-PD on Si displays potential application in the development of advanced optoelectronic devices.

9:00am **TF+EM+MI-TuM-4 Correlating the Optical Property Evolution in the Au-Ni Binary Thin Films: From Metastable Solid Solution to Phase Separated Alloy**, ***Robyn Collette***, *Y Wu, P Rack,* University of Tennessee Knoxville

Surface plasmon resonances can be sustained by metallic nanostructures and have been explored for potential optoelectronic device applications. Metallic alloys provide a pathway to tune the plasmonic response of a material. Additionally, alloying may allow for multifunctional materials to be realized. For example, Au-Ni alloys may combine the magnetic properties of ferromagnetic Ni with the plasmonic properties of Au. However, limited studies have been conducted on Au-Ni alloys for use in plasmonic devices. Since the behavior of the alloys depends on the structure, it is first critical to understand the relationship between the structure and the optical properties of the alloy.

In this study, the optical properties of Au$_{1-x}$Ni$_x$ alloy thin films are investigated by employing a combinatorial sputtering approach. The dielectric function is measured using spectroscopic ellipsometry and is correlated to the composition (energy dispersive x-ray spectroscopy), and phases present (x-ray diffraction). As-deposited alloys form a metastable solid solution, however, annealed alloys exhibited phase separation into Au-rich and Ni-rich phases due to the large miscibility gap in the Au-Ni material system. The optical properties are then rationalized by modeling the dielectric function of the solid solution alloys with a Drude-Critical Point analytical model. Lastly, the efficacy of the model is demonstrated which shows that the dielectric function of the phase separated alloys may be approximated using a composition-weighted average of two solid solution dielectric functions.

9:20am **TF+EM+MI-TuM-5 Integration of Electro-optically Active BaTiO$_3$ and Ba$_x$Sr$_{1-x}$TiO$_3$ with Buffered Si (001) by Chemical Methods**, ***John G. Ekerdt***, *B Edmondson, E Lin,* University of Texas at Austin; *S Kwon,* University of Texas at Dallas; *A Demkov,* University of Texas at Austin; *M Kim,* University of Texas at Dallas

Recent investigations into thin film BaTiO$_3$ (BTO) show it is a promising candidate for on-chip photonic devices due to its large linear electro-optic (EO) coefficient (r > 100-1000 pm/V) relative to more conventional photonic materials such as LiNbO$_3$ (~30 pm/V) or strained Si (~2 pm/V). However, such high coefficients are achieved only by costly and inherently un-scalable physical vapor deposition techniques. In recent studies, we have investigated chemical routes to the integration of electro-optically active BTO thin films with Si, which offer faster and more scalable methods of deposition. Specifically, atomic layer deposition (ALD) of 40 nm BTO films and chemical solution deposition (CSD) of 85 nm BTO films on SrTiO$_3$ (STO) templates on Si (001) prepared by molecular beam epitaxy (MBE) yield epitaxial BTO films with microstructure and defect nature markedly different from physical deposition techniques. Furthermore, we explored CSD of *c*-axis in-plane Ba$_x$Sr$_{1-x}$TiO$_3$, which is difficult to achieve by physical methods and offers unique insight into the EO behavior of this highly tunable dielectric. X-ray diffraction and scanning transmission electron microscopy confirmed epitaxial, distorted tetragonal structures with a range of structural defects, and electrical and electro-optical measurements showed diminished ferroelectricity and EO response compared to MBE-grown thin films or bulk BTO. ALD-grown films exhibited optical hysteresis with coercivity of ~10 kV/cm, an effective linear EO coefficient of 26 pm/V for 40 nm films, and leakage currents caused by oxygen vacancies. CSD-grown films did not show evidence of ferroelectric hysteresis but maintained EO response with a coefficient of 25 pm/V and had very low leakage current. Past reports of chemical vapor deposited films yielded an EO coefficient of 7 pm/V. These results provide further understanding into the relationship between film structure and linear EO behavior.

9:40am **TF+EM+MI-TuM-6 Nonlinear Optical Properties of TiO$_2$-based ALD Thin Films**, ***Theodosia Gougousi***, *R Kuis, I Basaldua, P Burkins, J Kropp, A Johnson,* University of Maryland, Baltimore County

Nonlinear materials in thin film form are highly desirable for the development of ultrafast all-optical system on-a-chip platforms, optical frequency converters and optical limiting applications. Conventional nonlinear optical (NLO) materials are usually cut from bulk crystals or are liquids that are not suitable for integration with the contemporary semiconductor industry process flow. The third order nonlinear response of ALD TiO$_2$-based films is investigated using thermally managed Z-scan technique. Some of the as-deposited films exhibit very high nonlinear response which is orders of magnitude higher than conventional nonlinear optical materials such as silica fibers and CS$_2$. Thermal treatment of the films at 450°C for 3 hours in an oxygen rich atmosphere affects the films' optical properties and results in the loss of the high nonlinear optical response. TiO$_2$ films deposited by Physical Vapor Deposition (PVD) from a 99.9% TiO$_2$ target at room temperature are used as control samples and their nonlinear optical response is found below the detection limit of the Z-scan setup. This extraordinary nonlinear optical behavior of the TiO$_2$ ALD films is linked to the presence of a very small at. % of TiN bonding in the film. We will present detailed characterization of these films by x-ray photoelectron spectroscopy, x-ray diffraction and UV-Vis absorption. The high level of control of the nonlinear index of refraction, n$_2$, using the deposition process coupled with the ability of ALD to coat nonplanar geometries with atomic level precision and the fact that these processes are CMOS compatible have the potential to provide a breakthrough in optical device design and applications.

11:00am **TF+EM+MI-TuM-10 Atomic Layer Deposition on Hexagonal Ge and SiGe Nanowires for Surface Passivation**, ***Willem-Jan Berghuis***, Department of Applied Physics, Eindhoven University of Technology, Postbus 513, 5600 MB Eindhoven, The Netherlands; *E Kessels,* Eindhoven University of Technology, The Netherlands, Netherlands; *J Haverkort, E Bakkers, A Dijkstra, E Fadaly, M Verheijen,* Eindhoven University of Technology, The Netherlands

Semiconductor nanowires (NWs) are nanoscale rods with a typical length of a few microns. They are made of materials such as Ge, Si, InP, GaAs. Due to their high aspect ratio, nanowires have a very high surface-to-volume-ratio, which leads to a large influence of the surface on their electronic and optical properties. Surface states facilitate recombination of electron-hole pairs, which reduces the photovoltaic conversion efficiency of NW solar cells [1] or which decreases the output of NW based LEDs or lasers. The surface can also induce space charge regions in the nanowires, which greatly affects their conductivity and which can be critical in for example sensing applications [2]. To reach the desired performance of nanowires in their applications, it is important to control the surface effects.

Atomic layer deposition (ALD) is a deposition technique that allows for preparation of ultrathin films with sub-nanometer thickness control and with an excellent conformality on high aspect ratio structures such as nanowire arrays. For these reasons ALD is a suitable technique to cover nanowires with thin films to control the surface properties.

Recently, nanowires have enabled the growth of Ge and SiGe in the hexagonal diamond crystal phase [3]. In contrast to the cubic crystal phase of these materials, the hexagonal crystal phase leads to a direct bandgap. The latter makes this material an interesting candidate to realize solid-state lasers that are compatible with the current silicon-based electronics. One of the important steps to accomplish this is to reduce the surface recombination losses; i.e. to passivate the surface.

The aim of this work is to explore the surface passivation of these hexagonal Ge and SiGe nanowires. We do so by covering the nanowires with ultrathin films of Al_2O_3 prepared by thermal and plasma-assisted ALD (PE-ALD). Secondly, we cover the wires with a stack of PO_x/Al_2O_3. The latter is a relatively new passivation scheme that has proven very successful for the surface passivation of InP nanowires [4] and Si wafers [5]. The change in photoluminescence (PL) of the nanowires as a function of the ALD films has been studied to assess the surface passivation and the influence of various pre- and post-treatments. Conformal coating of hexagonal Ge nanowires has been realized and we have observed an improvement of the photoluminescence for NWs covered with PE-ALD Al_2O_3 and PO_x/Al_2O_3.

11:20am **TF+EM+MI-TuM-11 Oxidation Studies of Silicon Germanium (SiGe) using In-Situ Steam Generated (ISSG) and Plasma Enhanced Atomic Layer Deposited (PEALD) Oxides**, ***Yi Song***, *S Siddiqui, C Durfee, A Pana, J Li, M Belyansky, S Naczas, E Stuckert, L Jiang, J Demarest, V Basker, D Guo, H Bu,* IBM Research Division, Albany, NY

SiGe is a versatile material for the semiconductor industry for sub-7 nm node technology development; it can be used as a high mobility channel material in FinFET, and as multiple sacrificial layers to form channel regions in gate all around (GAA) nanosheet device architecture. Understanding SiGe film oxidation is important for matching oxidation rates between SiGe layers with different Ge% in nanosheet applications [1]. In this paper, a study of ISSG (800 °C) and PEALD (room temperature to 300 °C) oxidation processes is performed on blanket $Si_{1-x}Ge_x$ films ranging from $x = 0.25$ to 0.80. We establish the boundaries of three distinct regions of oxidation behavior for the ISSG process (Region I: $0 < x < 0.5$, Region II: $0.5 < x < 0.67$, and Region III: $x > 0.67$). Historically, low Ge oxidation has been extensively studied [2-4]. Here, we show for Region I, the ISSG oxidation rate is very small (1.7 nm of oxide growth in 5 sec). The oxidation rate rapidly increases in Region II as x increases, where it reaches a maximum (13.8 nm in 5 sec) at the Region II/Region III boundary, then abruptly drops in Region III as x increases due to complete sublimation of Ge (see Figure 1). The abrupt increase in the ISSG oxidation rate between Regions I and II makes it difficult to match oxide thicknesses for the wide range of Ge% utilized by nanosheet device architecture. Therefore, we studied a lower temperature oxidation process (PEALD) which has a lower oxidation rate. We found that PEALD oxidation rates are unchanged across the Region I/II boundary, even for higher temperatures up to 300 °C as shown in Figure 2. This enables oxide thickness matching for a wide range of Ge%. These results are applicable to the development of various nanotechnologies such as nanosheet and high mobility channel FinFET devices.

11:40am **TF+EM+MI-TuM-12 Precision Defect Engineering of Metal/Insulator/Metal (MIM) Diodes using Localized ALD Transition Metal Impurities in Al_2O_3 Tunnel Barriers**, ***Konner Holden***[1], *Y Qi, J Conley, Jr.,* Oregon State University

Thin film MIM tunnel diodes are receiving increased interest for high-speed applications such as THz detection and rectenna based energy harvesting. Traditionally, current density vs. field (J-$\mathcal{E}$) asymmetry ($ƒ_{asym} = J^-/J^+$) with MIM diodes has been achieved through metal work function differences ($\Delta\Phi_M$). Recently, nanolaminate insulator tunnel barrier MIIM diodes enabled by ALD showed improved $ƒ_{asym}$, non-linearity, and responsivity at low voltage by step tunneling through the wider bandgap (E_G) insulator to the conduction band of the narrow E_G insulator.[1] *Intrinsic defects* present in narrow E_G insulators were later demonstrated to further improve low $\mathcal{E}$ asymmetry via defect enhanced direct tunneling, when paired with an insulator dominated by tunneling.[2,3] In this work, we investigate the impact of localized *extrinsic defects* by using ALD to intentionally introduce Ni at precise intervals in an Al_2O_3 tunnel barrier.

ALD of Al_2O_3 on TiN was performed at 200 °C using TMA and H_2O. Five samples were prepared in which a 100 cycle Al_2O_3 ALD sequence was interrupted by two cycles (c) of $Ni(^{tBu2}DAD)_2$ and O_3 after 25, 50, 75, and every 25 c of Al_2O_3. As-deposited MIM devices were tested with bias applied to an Al top electrode (Fig. 1).

DC J-$\mathcal{E}$ sweeps of the 100 c device show Fowler-Nordheim tunneling (FNT) at high $\mathcal{E}$, with $ƒ_{asym} > 1$ due to $\Delta\Phi_M \approx 0.2$ eV (Fig. 1). The addition of Ni cycles in all cases leads to an increase in J at low $\mathcal{E}$ vs. the 100 c Al_2O_3 device, suggesting defect related conduction. At high $\mathcal{E}$, however, J of all Ni devices is lower than the 100 c device, suggesting suppression of FNT. The 25/2/75 and 75/2/25 (Al_2O_3/Ni/Al_2O_3) devices show $ƒ_{asym}$ *opposite* of the 100 c device, while the 50/2/50 and 25/(2/25)x3 devices are roughly symmetric (Fig. 1). The greater reduction in J at large negative $\mathcal{E}$, $ƒ_{asym}$ reversal, and reduced J-$\mathcal{E}$ slope for the 25/2/75 and 75/2/25 devices suggest that FNT is suppressed more for emission from the smaller Φ_M electrode (Al) than for TiN. FNT suppression appears greatest for the 75/2/25 device in which Ni is closest to the Al, pointing to an increase in effective barrier height, likely due to negative charge in the Al_2O_3. Capacitance (C) *vs.* $\mathcal{E}$ sweeps (Fig. 2) reveal a positive voltage shift in C_{min} for all Ni devices, consistent with negative charge.

The asymmetry reversal demonstrates the possibility of precision defect engineering of MIM tunnel devices using ALD. An in-depth discussion of J-$\mathcal{E}$ and C-$\mathcal{E}$, temperature-*IV*, frequency-*CV*, other impurities, and annealing will be presented.

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12:00pm **TF+EM+MI-TuM-13 Improvement in the Electrical Characteristics of a-ZTO based TFTs *via* Microwave Assisted Annealing of Channel Layer**, ***Sunil Uprety***, *M Khanal, H Lee, S Sarwar,* Auburn University; *A Subramanian,* Stony Brook University; *E Hassani, T Oh, X Zhang,* Auburn University; *C Nam,* Brookhaven National Laboratory; *M Park,* Auburn University

In this research, we have investigated the effect of microwave-assisted annealing of amorphous zinc tin oxide (a-ZTO) channel layers on the electrical characteristics of the thin film transistors (TFTs). A multi-stacked a-ZTO layer was deposited on the oxidized Si wafer using sol-gel process. The precursor solution was prepared by dissolving zinc acetate dihydrate and tin chloride dihydrate into methoxyethanol. The solution was spin coated and calcined in a hot plate at 285°C. The as-calcined a-ZTO wafers were microwave annealed. The microwave (MW) annealing was carried on a commercial microwave oven at different power levels with the sample placed in a kiln which acts as a susceptor. The films remained amorphous even after MW annealing, which was evidenced by X-ray diffraction. The devices were fabricated using the microwave-annealed and as-calcined samples. Hall measurement is being carried out to study the concentration and mobility of charge carries. The performance of the TFTs with as-calcined and MW annealed channel layers were compared. Improvement in the electrical characteristics of the TFTs with MW annealed films were noted. It is believed that the microwave irradiation may promote the enhancement of the electrical characteristics of TFTs. Further research is being pursued to elucidate the role of microwave annealing in improvement of the device performance.

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[1] **TFD James Harper Award Finalist**

2D Materials
Room A216 - Session 2D+EM+MI+NS-TuA

Properties of 2D Materials including Electronic, Magnetic, Mechanical, Optical, and Thermal Properties II

Moderator: Roland Wiesendanger, University of Hamburg, Germany

2:20pm **2D+EM+MI+NS-TuA-1 Boundary Conditions for a Continuum Model of Lateral Interfaces in Transition Metal Dichalcogenides*, Kaelyn Ferris,*** Ohio University

Tight-binding models of in-plane, lateral heterostructures of commensurate transition-metal dichalcogenides (TMD), such as MoS_2-WS_2 and $MoSe_2$-WSe_2 have demonstrated the appearance of laterally localized effective one-dimensional interfacial and edge states with unique features. These states lie within the band gap of the bulk structure and may provide a stable, tunable one-dimensional platform for possible use in exploring Majorana fermions, plasma excitations, and potential spintronics applications [1]. Motivated by the possible versatility of these modes in a variety of 2D systems, we now explore their appearance in continuum model descriptions of effective massive Dirac systems at low energy. We use different k*p models to characterize TMD nanoribbons and analyze proposals for the appropriate boundary conditions at lateral interfaces with various terminations. In particular we examine an *M*-Matrix approach [2] and envelope function approximation to obtain suitable boundary conditions.

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[2] C. G. Peterfalvi et al., Phys. Rev. B **92**, 245443 (2015).

2:40pm **2D+EM+MI+NS-TuA-2 Resolving the Structural and Electronic Properties of Graphene/Ge(110)*, Luca Camilli,*** Technical University of Denmark, Denmark*; M Galbiati,* Technical University of Denmark*; L Persichetti, M De Seta,* Università degli Studi Roma Tre, Italy*; F Fabbri,* Italian Institute of Technology, Italy*; A Scaparro,* Università degli Studi Roma Tre, Italy*; A Notargiacomo,* Centro Nazionale di Ricerca, Italy*; V Miseikis, C Coletti,* Italian Institute of Technology, Italy*; L Di Gaspare,* Università degli Studi Roma Tre, Italy

Unraveling the structural and electronic properties of the interface between graphene and conventional semiconductors is critical to enable novel graphene-based applications [1].

In this framework, the graphene/Ge(110) system has since last year received unprecedented attention [2-6]. Notably, graphene can be grown via chemical vapor deposition directly on the surface of germanium, similarly to the case of graphene grown on metals [7]. From a structural point of view, the graphene/Ge system is very dynamic, and the Ge surface has been shown by scanning tunneling microscopy (STM) studies to undergo a number of changes (i.e., reconstructions). However, the conclusions drawn in those studies do not always agree, probably also due to the strong dependence of the STM images on the applied voltage bias that makes comparison between different images rather difficult. In Ref. [6], for instance, the authors report three different surface reconstructions that are driven by thermal annealing, while the authors in Ref. [4] find only the unreconstructed surface and a (6x2) reconstruction, which again can reversibly change to unreconstructed surface after annealing at high temperature in hydrogen.

In this study, we aim at resolving the rich phase diagram of the Ge surface protected by graphene. We carry out annealing of the sample at different temperatures, and use a low-temperature STM to investigate the surface structure with atomic precision. At each stage, images at different applied biases are collected in order to allow a more straightforward comparison of the results.

Moreover, we perform electron energy loss spectroscopy (EELS) and scanning tunneling spectroscopy (STS) at temperature below 10 K to shed light on the electronic properties of the graphene/Ge interface, and to get more insights into their interaction.

Finally, we also show through a combination of STM and Raman spectroscopy that graphene can protect the germanium surface from oxidation even after continuous exposure to ambient conditions for more than 12 months, which is surprisingly a far more efficient protection than that offered by graphene on metals [8, 9].

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3:00pm **2D+EM+MI+NS-TuA-3 Array of Strain Induced Quantum Dots in Graphene*, Md Tareq Mahmud,*** *N Sandler,* Ohio University

Local Gaussian-shaped deformations induce strain fields that are represented by scalar and vector potentials in a continuum model description of electron dynamics in graphene. The ubiquitous strain changes the charge distribution in a very peculiar way, introducing a sublattice symmetry breaking, as has been reported in the literature. This feature can be exploited to design specific charge profiles by combining several deformations. Naturally, a combination of two or more is expected to introduce interference effects that can enhance charge accumulation in specific regions. We have investigated the effects of two overlapping deformations with different separations on the local density of states (LDOS). We showed that the overlap term can enhance the LDOS leading to stronger charge confinement in certain regions. Motivated by the work of Mason et. al (2018) we have extended these studies to a closed pack structure with a unit cell of 3 distinct deformations. This arrangement can be extended by symmetry to a lattice superstructure, thus creating a periodic array of confined charge regions, i.e, quantum dots. This array can be tailored by appropriately choosing the parameters of the deformations and their distances. The total charge distribution in these systems is similar to those observed in twisted bilayer systems, known as 'Moire patterns'. We discuss optimal tuning of deformations to control the physical properties of these graphene devices.

3:20pm **2D+EM+MI+NS-TuA-4 Ultrafast Spin and Charge Dynamics in Monolayer WSe_2-Graphene Heterostructure Devices*, Michael Newburger,*** *K Luo,* The Ohio State University*; K McCreary,* U.S. Naval Research Laboratory*; I Martin, E McCormick,* The Ohio State University*; B Jonker,* U.S. Naval Research Laboratory*; R Kawakami,* The Ohio State University

Monolayer transition metal dichalcogenides (TMDs) have attracted attention due to their long spin/valley lifetimes and ability to couple the helicity of light to spin/valley polarization. Additionally, a strength of TMDs lies in their ability to complement other materials, such as graphene, by acting as a means of optical spin injection or proximity coupling. Recently, multiple groups have demonstrated proximity mediated charge transfer and optical spin injection in TMD/graphene heterostructures. However, the spin transfer dynamics across a TMD/graphene interface remain largely unexplored.

Here we utilize time-resolved Kerr rotation (TRKR) microscopy to image the spatial dependence of spin/valley dynamics in monolayer WSe_2/graphene heterostructure devices. Spatial maps demonstrate long-lived spin/valley lifetimes on the bare WSe_2 but reveal a quenching of spin-valley signal at the WSe_2/graphene interfaces. Time delay scans show these interface lifetimes to be quenched up to 3 orders of magnitude in comparison to bare WSe_2. Furthermore, photoluminescence mapping exhibits quenching at the interfaces while photoconductivity is enhanced in these regions, demonstrating efficient charge transfer from WSe_2 to graphene. Consequently, we attribute the ultrafast spin/valley quenching to the transfer of spin information by conducted charge carriers.

4:20pm **2D+EM+MI+NS-TuA-7 Spatially Selective Enhancement of Photoluminescence in MoS by Exciton-Mediated Adsorption and Defect Passivation*, Saujan V. Sivaram,*** *A Hanbicki, M Rosenberger, G Jernigan, H Chuang, K McCreary, B Jonker,* U.S. Naval Research Laboratory

Monolayers of transition metal dichalcogenides (TMDs) are promising components for flexible optoelectronic devices due to their direct band gap and atomically thin nature. The photoluminescence (PL) from these materials is often strongly suppressed by non-radiative recombination mediated by mid-gap defect states. Here, we demonstrate up to a 200-fold increase in PL intensity from monolayer MoS_2 synthesized by chemical vapor deposition (CVD) by controlled exposure to laser light in ambient. This spatially resolved passivation treatment is air and vacuum stable. Regions unexposed to laser light remain dark in fluorescence despite continuous impingement of ambient gas molecules. A wavelength dependent study confirms that PL brightening is concomitant with exciton generation in the MoS_2; laser light below the optical band gap fails to produce any enhancement in the PL. We highlight the photo-sensitive nature of the process by successfully brightening with a low power broadband white light source (< 10 nW). We decouple changes in absorption from defect passivation by examining the degree of circularly polarized PL. This measurement, which is independent of exciton generation, confirms that laser brightening reduces the rate of non-radiative recombination in the MoS_2. A series of gas exposure studies demonstrate a clear correlation between PL brightening and the presence of water. We propose that H_2O molecules passivate sulfur vacancies in the CVD-grown MoS_2, but require photo-generated excitons to overcome a large adsorption barrier. This work represents an important step in understanding the passivation of CVD-synthesized TMDs and demonstrates the interplay between adsorption and exciton generation.

This research was performed while S.V.S and M.R.R held a National Research Council fellowship and H.-J.C. held an American Society for Engineering Education fellowship at NRL.

4:40pm **2D+EM+MI+NS-TuA-8 Strained Graphene in the Quantum Hall Regime: Valley Splitting and Extra Conducting Channels***, **Daiara Faria,*** Ohio University / Universidade do Estado do Rio de Janeiro*; C León,* Brigham Young University*; L Lima,* Universidade Rural do Rio de Janeiro, Brazil*; A Latgé,* Universidade Federal Fluminense, Brazil*; N Sandler,* Ohio University

The coupling between electronic and mechanical properties in 2D materials has become an important tool to control valleytronics. Graphene experiments have been reported with common deformations such as membrane bending that induces strain in the samples [1]. It has also been shown that strain affects charge distributions and graphene transport properties. Motivated by these responses, we have studied the effect of folds and wrinkles in graphene. New 'edge'-like states along the graphene folded region, that are valley polarized, were found and explored [2]. To take advantage of the existence of these new states, it would be desirable to separate their contribution from the continuum extended states that make graphene a semimetal.

Here we present a theoretical study of folds effects on a graphene membrane in the quantum Hall regime. We show that the addition of an external magnetic field allows the isolation of the valley polarized edge states in energy and in real space. Local density of state calculations in the deformation region predict the valley split peaks, as observed in recent experimental [3]. Using recursive Green's function method, we are able to reveal new extra conducting channels due to the "new edges" at the deformation region. These extra conducting channels could be detected in transport measurements.

A discussion is presented to bring attention on the role of the deformation parameters on the graphene quantum Hall regime and their relations with the magnetic lengths. With this in mind, we perform an analytic study based on the continuum (Dirac) description of electrons in graphene. In this model, the deformation is considered as a perturbation to the Landau Level states. The results show the existence of two different regimes, characterized by the ratio between the magnetic length and the deformation width ($\gamma = l_B/b$). For $\gamma<1$ the magnetic confinement allows the electrons to follow the strain potential profile. In this regime, the spatial separation between the polarized currents is larger. This could encourage the design of devices where contacts can efficiently detect these polarized currents.

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5:00pm **2D+EM+MI+NS-TuA-9 Unraveling the Novel Quantum Phenomena in Two-dimensional Materials using Transport and Photoemission Spectroscopy***, **Jyoti Katoch,*** Carnegie Mellon University **INVITED**

The extreme surface sensitivity of two-dimensional (2D) materials provides an unprecedented opportunity to engineer the physical properties of these materials via changes to their surroundings, including substrate, adsorbates, defects, etc. In addition, 2D materials can be mechanically assembled layer-by-layer to form vertical or lateral heterostructures, making it possible to create new material properties merely by the choice of the constituting 2D layers and the relative twist angle between them. In this talk, I will discuss our recent transport [1] and photoemission [2, 3] results that shed light on the intricate relationship between controlled external perturbations, substrate, and electronic properties of 2D materials. I will show that the decoration of the 2D materials with adatoms, such as sub-lattice selective atomic hydrogenation of graphene and alkali metal doping of single layer WS_2 can be utilized to tailor electronic properties and induce novel quantum phenomena in 2D landscape.

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5:40pm **2D+EM+MI+NS-TuA-11 Electronic Properties and Charge Density Wave Transition in Single-layer VSe_2***, **Kien Nguyen-Cong**, P Neto, M Batzill, I Oleynik,* University of South Florida

Single-layer VSe_2 has been recently attracted attention due to experimental observations of ferromagnetism and charge density wave (CDW) transition. There are controversies from both theory and experiment concerning ferromagnetism in both bulk and single layer VSe_2.In addition, CDW transition in VSe_2 is not well understood. In this work, structural, electronic, magnetic and CDW properties of this system are investigated using first-principle calculations. The calculated electronic structure is compared with recent APPRES measurements and conclusions concerning its magnetic state are made. The calculated phonon spectra are used in investigation of CDW transition mechanism. Crystal structure of the CDW state is determined using the evolutionary crystal structure prediction combined with lattice dynamics.

6:00pm **2D+EM+MI+NS-TuA-12 Tunable Band Gap and Thermal Conductivity Measurements of Monolayer $MoSe_2$ by S Incorporation***, **Shyama Rath**, V Singh,* University of Delhi, India

Monolayer $MoSe_2$ was grown on insulating SiO2/Si substrates by chemical vapor deposition. Scanning electron microscopy and optical contrast images were used to determine the domain size, morphology, and the number of layers. The crystallinity, and thickness of the synthesized domains were determined by Raman spectroscopy. The band gap was determined from Photoluminescence (PL) spectroscopy. The PL emission was absent for more than 4 layers, and the peak position varied from 1.48 eV for 4 layers to 1.55 eV in the monolayer limit. Sulphur incorporation was done to obtain MoS_xSe_{2-x} so as to obtain a further tunability of the bandgap. The band gap changes from 1.55 eV for monlayer $MoSe_2$ to 1.64 eV for monolayer $MoS_{0.32}Se_{0.68}$. Further, larger area domains were achieved in the alloy as compared to binary. The thermal conductivity of the monolayer $MoSe_2$ and MoS_xSe_{2-x} were determined from temperature-dependant Raman spectroscopy.

Electronic Materials and Photonics Division
Room A214 - Session EM+OX+TF-TuA

Nikolaus Dietz Memorial Session: Wide and Ultra-wide Band Gap Materials and Devices

Moderators: Seth King, University of Wisconsin - La Crosse, David Aspnes, North Carolina State University

2:20pm **EM+OX+TF-TuA-1 Nitride-Based Semiconducting Materials: A Long Pathway to Advanced Nuclear Detection Capabilities***, **Vincent Woods**, L Hubbard,* Pacific Northwest National Laboratory*; Z Sitar,* North Carolina State University*; A Kozhanov,* Georgia State University **INVITED**

This energetic talk will focus primarily on the development of advanced nitride-based avalanche photodiode devices but will also highlight the many contributions that Nikolaus Dietz made to the field of real-time optical characterization, materials development and advanced growth techniques. Iterative development and advances in growth techniques and characterization have allowed sufficient improvement in materials quality to show demonstrable g ain in Avalanche Photodiode Detector (APD) device structures currently being produced for nuclear detection applications. This contribution will present the structural and optoelectronic properties of GaN/AlGaN heterostructures grown by Metal Organic Chemical Vapor Deposition (MOCVD) on AlN, GaN and sapphire templates/substrates. The target parameters for the materials heterostructures have been modeled for utilization in APD structures operating in the UV region. Optical modeling has improved absorption within the heterojunction as well as maximized light trapping within the device. Electronic modeling has determined the optimal dopant concentrations for maximum impact ionization rate, as well as tolerance to defects and unintentional doping. This application required advances in the defect densities, surface morphology, and interfaces. Surface morphological and structural properties of the GaN/AlGaN heterostructures are analyzed by Atomic Force Microscopy (AFM), and high resolution transmission electron microscopy (TEM). Recent results related to the gain of the final APD device will be presented.

3:00pm **EM+OX+TF-TuA-3 New Mg-based Ternary Nitrides for Wide Band Gap Device Applications***, K York, R Makin III,* ***Steven Durbin,*** Western Michigan University*; R Reeves,* University of Canterbury, New Zealand*; N Senabulya, R Clarke,* University of Michigan

There continues to be significant interest in discovering viable alternatives to the traditional indium- and gallium-containing semiconductors, especially the nitrides, given the cost of the metallic constituents. The general family of ternary heterovalent semiconductors provides a number of interesting candidates, and considerable progress with a number of them has been made in the last several years. In addition to realizing $ZnSnN_2$ in thin film form using plasma-assisted molecular beam epitaxy (PA-MBE), we have recently demonstrated for the first time that the previously hypothetical wide band gap semiconductors $MgSnN_2$ (Eg ~ 3.4 eV) and $MgGeN_2$ (Eg ~ 5.1 eV) can also be grown. Zinc tin nitride ($ZnSnN_2$) has received considerable interest recently as a potential earth-abundant element based compound semiconductor for photovoltaic device applications. Its constituent elements are inexpensive, readily available in high-purity form, non-toxic, and both zinc and tin benefit from mature recycling infrastructure. We have studied the growth of crystalline thin films of all three ternary heterovalent compounds with a view to understand their optical and electronic properties. We have demonstrated that the optical band gap energy exhibits a strong correlation with the ordering of the cation sublattice, and used this to determine the full range of possible band gap energies. Cation ordering is quantified through the long-range order parameter, which can be measured by x-ray diffraction, Raman spectroscopy, or in-situ reflection high-energy electron diffraction. All three materials can be successfully grown on (111) YSZ substrates, which represents a nontrivial lattice mismatch. We are able to control the cation ordering over essentially the entire range of possible long-range order parameter values through systematic variation of PA-MBE growth parameters, and have demonstrated reproducibility of a few percent.

3:20pm **EM+OX+TF-TuA-4 Low Temperature Growth of InN by Atomic Layer Epitaxy***,* ***Charles R. Eddy, Jr.,*** U.S. Naval Research Laboratory*; S Rosenberg, J Woodward,* American Society for Engineering Education (residing at U.S. Naval Research Laboratory)*; K Ludwig,* Boston University*; N Nepal,* U.S. Naval Research Laboratory

Wurtzite indium nitride (InN) has direct bandgap of about 0.7 eV with large phonon gap and is an attractive semiconductor material for application in various areas, e.g. optical, electrical, optoelectronic, and spintronic device technologies [1]. InN and its alloys with GaN and AlN (III-N) have therefore found application in a variety of technologies such as high power transistors, emitters, detectors, and solar-cells. The relatively high growth temperature of common III-N synthesis techniques has impeded further development and application of the materials due to challenges with miscibility gaps and strain related to thermal expansion mismatch with non-native substrates. To address these challenges, plasma assisted atomic layer epitaxy (PA-ALEp) offers a new approach to low temperature III-N growth and can be used to epitaxially grow InN by using alternative pulses of trimethylindium and nitrogen plasma [2]. We report on development of the PA-ALEp process for InN growth on sapphire and gallium nitride substrates demonstrating the self-limited growth windows as a function of temperature and pulse durations in the process. We benchmark the quality of our films compare to those grown by Dietz et al. by high pressure CVD [3]. The process produces quality, crystalline semiconductor films with properties comparable to those grown by conventional methods at temperatures roughly 2X higher. Beyond that, the PA-ALEp process affords realization of InN containing ternary nitrides with aluminum and gallium that are not possible with conventional growth methods. Further, the unique, non-thermal equilibrium process enables realization of cubic (rock salt) phases on InN. In order to better understand nucleation and growth mechanisms involved in the PA-ALEp process, we employ in situ X-ray scattering methods using synchrotron radiation. We have determined that the growth proceeds largely by a Stranski-Krastinov process on either sapphire or gallium nitride. Further, we have investigated the impact of components of the PA-ALEp cycle on the growth process [4], in particular the plasma pulse time. Here we see that pulse time can affect the nature of nucleation from bimodal nucleation to single mode nucleation to degraded growth as pulse time increases from 15 seconds to 30 seconds. These and other nucleation and growth behaviors will be highlighted.

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4:20pm **EM+OX+TF-TuA-7 Stochiometry- and Orientation-Dependent Native Point Defects of MOCVD-Grown $ZnGeN_2$ Films***,* ***Micah Haseman,*** *D Ramdin, R Karim,* The Ohio State University*; D Jayatunga,* Case Western Reserve University*; H Zhao,* The Ohio State University*; K Kash,* Case Western Reserve University*; L Brillson,* The Ohio State University

Heterovalent ternary II-IV-nitrides like $ZnGeN_2$ are attracting increased interest due to their close relation to technologically important III-nitrides such as GaN. Unlike many III-nitrides, the constituents of $ZnGeN_2$ are more earth-abundant with potential for more versatile optoelectronic lattice matching. Essential to II-IV-nitride device application is the control of native point defects and subsequent manipulation of doping and carrier compensation. In many wide band gap binary semiconductors such as GaN or ZnO the most thermodynamically stable defects are cation or anion vacancies whereas stable defects in ternary alloys may include antisites, interstitials, and their complexes as well as H interstitials and complexes. Thus identification of native point defects in $ZnGeN_2$ and other ternaries can be challenging. Using depth-resolved cathodoluminescence spectroscopy (DRCLS), we have observed multiple deep level defects in MOCVD-grown $ZnGeN_2$ films. Excitation depths obtained via Monte Carlo simulations for varying incident electron beam energies provide depth-resolution for the cathodoluminescence spectra which reveal defects that extend throughout the deposited $ZnGeN_2$ film and are not localized near the free surface nor the film-substrate interface, therefore, unless these defects are unintentional impurities, they must be native point defects. Density functional theory (DFT) predicts the most thermodynamically stable native point defects are in fact Zn_{Ge} and Ge_{Zn} antisites and the n-type nature of the films studied suggests that Zn_{Ge} acceptor is the most favorable defect to form [1]. We used off-stoichiometric films to identify luminescence features due to gap state transitions from specific defects. For Zn-rich films (Zn/Ge = 1.15), we observe an additional defect feature at 2.4 eV corresponding to a near mid-gap state. DFT band structures for $ZnGeN_2$ show that Zn_{Ge} antisites create gap states just below mid-gap, consistent with the n-type Fermi level and with the Zn-rich films. In addition, we observe strong variation in these mid-gap states with Al_2O_3 vs GaN substrate growths as well as an Al_2O_3 orientation dependence. DRCLS's ability to probe electronic structure on a near-nanometer scale enables us to probe defect variations with stoichiometry as growth conditions are varied within the outer tens of nanometers - a nanoscale testbed to identify defects. Identifying and controlling such defects using growth processes can enable advances in $ZnGeN_2$ for next generation electronic device applications. The authors gratefully acknowledge support from NSF grants DMR-18-00130 and DMREF 1533957.

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4:40pm **EM+OX+TF-TuA-8 Low-temperature Growth of Wide Bandgap Nitride and Oxide Thin Films via Plasma-assisted Atomic Layer Deposition: Influence of rf-plasma Source and Plasma Power***,* ***Necmi Biyikli****, S Ilhom, A Mohammad, D Shukla,* University of Connecticut

Plasma-assisted atomic layer deposition (PA-ALD) provides an alternative way to grow wide bandgap materials at substantially reduced substrate temperatures (lower than 400°C) when compared to conventional epitaxial growth techniques. While majority of the published literature indicate polycrystalline or amorphous films, recent results depict preferred crystal orientation and even single crystalline nitride and oxide films obtained mainly by delicate substrate in-situ cleaning and careful plasma condition tuning and optimization.

In this talk, we will give an overview of the current state-of-the-art in PA-ALD research on wide and ultra-wide bandgap semiconductors, focusing mainly on wide bandgap III-nitrides (AlN, GaN) and III-oxides (Ga_2O_3). Subsequently, we'll share our recent research efforts on growing crystalline GaN and Ga_2O_3 thin films via PA-ALD utilizing two different plasma sources: inductively coupled plasma (ICP) and capacitively-coupled hollow-cathode plasma (CCHCP) source. We show that for III-nitride films, CCHCP source provides significant improvement in terms of oxygen impurity incorporation and structural film quality, while using a compact vacuum reactor with reduced source-to-substrate distance leads to reduced plasma power levels needed for self-limiting growth saturation curves. Both sources will also be compared in terms of film quality for ultra-wide bandgap Ga_2O_3.

We will present how the choice of plasma source and rf-plasma power affects the structural, chemical, optical, and electrical properties of the grown wide bandgap nitride and oxide films. Detailed x-ray diffraction

(XRD), x-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM), spectroscopic ellipsometer (SE), Hall measurements (HM) results and analyses will be presented. In addition to these ex-situ characterization results, we'll provide our real-time in-situ ellipsometric film growth monitoring results which provide valuable information about the single chemisorption, ligand-exchange/removal, and nitrogen/oxygen incorporation reactions.

We'll present proof-of-concept electronic and opto-electronic device demonstration based on GaN and Ga2O3 films grown via PA-ALD and will conclude with a future outlook in terms of how to further improve material quality and device performances.

5:00pm **EM+OX+TF-TuA-9 Wide Bandgap Dilute Magnetic Semiconductors for Room Temperature Spintronic Applications**, *V Saravade, A Ghods,* Missouri University of Science and Technology, Rolla, MO, USA*; N Ben Sedrine,* Universidade de Aveiro, Portugal*; C Zhou, **Ian Ferguson**,* Missouri University of Science and Technology **INVITED**

Wide bandgap dilute magnetic semiconductors (DMS) are promising materials for spintronic applications due to their theoretically predicted and experimentally observed ferromagnetic properties at room temperature (RT) [1]. Spintronics is an enabling technology for devices that will meet current and future computing needs through quantum computing, neuromorphic applications, and artificial intelligence.

Gallium nitride doped with rare earth or transition metals have exhibited ferromagnetic behavior for spintronic applications although its mechanism is still not well understood [1]. In order to build spin-based devices, it is necessary to understand, control, and manipulate their magnetic properties. MOCVD-grown GaGdN shows RT ferromagnetism as evidenced in vibrating sample magnetometry and anomalous Hall Effect (AHE) measurements. Also, AHE measurement showed that the mechanism for the ferromagnetism is intrinsic and likely mediated by free carriers, which is conducive for spintronic applications [2]. However, ferromagnetism is only observed with a Gd precursor, (TMHD)$_3$Gd, which contains oxygen in its organic ligand that appears to be incorporated into the GaGdN. As per density functional theory calculations, oxygen and carbon could introduce deep localized states close to the Fermi level in GaGdN that couple with Gd states to render ferromagnetism [3, 4]. To achieve a clarity and control of this phenomenon, O and C are intentionally implanted into GaGdN grown using oxygen-free Cp$_3$Gd source. In this case, as-grown GaGdN is not ferromagnetic, but post-implantation with O or C does result in ferromagnetism. X-ray diffraction exhibits low damage and good crystal quality for the implanted GaGdN with peak shifts as compared to the GaGdN before implantation, showing signs of O or C incorporation. Annealing the implanted GaGdN activates the dopant, improves the crystal quality, and shows clear signs of AHE. This indicates that the intrinsic and potentially free carrier-mediated RT ferromagnetism in GaGdN is activated by band states introduced by O or C. A better understanding of the mechanism for RT ferromagnetism will enable using these materials to build spintronic devices, and processors for high speed computing applications.

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5:40pm **EM+OX+TF-TuA-11 Processing and Characterization of Schottky and Ohmic contacts on (100) β-Ga$_2$O$_3$**, ***Luke Lyle**, K Jiang, E Favela, D Moody, T Lin, P Chung,* Carnegie Mellon University*; K Das,* North Carolina State University*; Z Galazka, A Popp, G Wagner,* Leibniz-Institut für Kristallzüchtung, Germany*; L Porter,* Carnegie Mellon University

Over the past decade beta-gallium oxide (β-Ga$_2$O$_3$) has accrued increased interest due to its ultrawide bandgap of around 4.6 eV, superior figures of merit for numerous electronic and optoelectronic applications, and the ability to produce single-crystal melt-grown substrates. Considering these factors, β-Ga$_2$O$_3$ has been primarily pursued for applications as high-power electronics, of which the understanding and development of Schottky and ohmic metal contacts is critical. In this study we characterized the electrical properties of electron-beam evaporated Ni, Mo, Au and other metal Schottky contacts to (100) β-Ga$_2$O$_3$ substrates. Prior to deposition of the metals, the Ga$_2$O$_3$ surface was cleaned via a 10% HCl solution followed by a clean in boiling 30% H$_2$O$_2$ solution at 85°C. Ti/Au was deposited via electron-beam evaporation and annealed at 400°C in an Ar atmosphere for use as ohmic contacts. The ideality factors, barrier heights, and doping densities were calculated from I-V and C-V measurements, which showed excellent agreement in most cases; I-V-T measurements are also planned as a complementary method to determine electrical transport behavior as a function of temperature. From our measurements it was observed that the Schottky barrier heights tended to increase as a function of the metal workfunction. These results are in contrast to our prior measurements of Schottky contacts on (-201) β-Ga$_2$O$_3$, which showed little to no correlation between Schottky barrier height and metal workfunction. In this presentation we will compare the electrical behavior of the various metal contacts on (100) β-Ga$_2$O$_3$, including the extracted ideality factors (~1.05–1.2) and Schottky barrier heights (~0.9–2 eV). The results will be discussed in the context of important processing conditions, as well as structural, optical, and morphological characteristics of (100) and (-201) -Ga$_2$O$_3$ substrates as determined from x-ray diffraction, UV-visible spectroscopy, atomic force microscopy, and other techniques.

6:00pm **EM+OX+TF-TuA-12 III-Nitrides: Enabling Applications with Wide to Ultra-Wide Bandgap Materials and Devices**, ***Erica Douglas**, A Baca, B Klein, A Allerman, A Armstrong, A Colon, C Stephenson, R Kaplar,* Sandia National Laboratories

Though now commercially available, wide band gap semiconductors (WBG) such as GaN were pursued due to immense potential for high frequency, light-emission, and power electronic applications. Due to high breakdown voltages, which have been achieved due in part to intrinsic material properties and device engineering, as well as low on-state resistance, wide bandgap semiconductors have found significant success in the commercial application regime. The critical electric field that a material can withstand can be significantly increased through bandgap engineering due to critical field scaling as $E_g^{2.5}$ [1]. Thus, moving from WBG materials with bandgaps ~3 eV, to UWBG with bandgaps above 3.4 eV, alloying GaN with Al can increase the bandgap from 3.4 eV (GaN) to 6.2 eV (AlN) and result in a critical electric field approaching 5X that of GaN.

Since the first AlGaN-channel transistor was reported in 2008 [2], development and progress on devices with increasing Al content has been pursued, including high electron mobility transistors with channel concentrations as high as 85% Al [3]. Though a corollary can be drawn to GaN, there are still a significant number of challenges to overcome for AlGaN-channel devices, ranging from epitaxial growth to fabrication. This talk will describe the latest results at Sandia National Laboratories in AlGaN-channel HEMTs, including recent advances in: enhancement-mode operation, current density, device performance over temperature, and RF operation.

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.

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Complex Oxides: Fundamental Properties and Applications Focus Topic
Room A220-221 - Session OX+EM+HC+MI+NS+SS+TF-TuA

Complex Oxides: Catalysis, Dielectric Properties and Memory Applications

Moderators: Alexander Demkov, University of Texas at Austin, Jeffry Kelber, University of North Texas

2:20pm **OX+EM+HC+MI+NS+SS+TF-TuA-1 Novel Multiferroic and Ferroelectric Ferrite Thin Films**, ***Peter A. Dowben**, C Binek, X Xu,* University of Nebraska-Lincoln **INVITED**

Ferroelectricity and ferromagnetism are foundational to numerous technologies, yet the combination of ferroelectricity and ferromagnetism, namely multiferroicity, may be even more desirable. Multiferroic materials are believed to be a route to voltage controlled spintronic devices. Yet very few single phase materials are known to be ferroelectric and ferromagnetic at the same time, i.e. multiferroic. Even fewer materials are fewer materials are magneto-electric, that is to say materials with magneto-electric coupling, i.e. voltage control of magnetization, but without separate order parameters for magnetism (or antiferromagnetism) and ferroelectricity. This talk will review the electronic structure of the tri-rutile magneto-electric antiferromagnets, like Fe_2TeO_6, as well as rare earth ferrites like $ReFeO_3$ (Re = rare earth) stabilized in the hexagonal phase. Both types of materials are frequently antiferromagnetic, and, in principle, both can exhibit magneto-electric coupling. The surface termination affects the measured spin polarization of the surface and the interface with other materials. This will have a significant influence on the voltage control of magnetization. We have investigated the structural and electronic properties at the surface of these more unusual multiferroic materials using angle-resolved x-ray photoemission spectroscopy (ARXPS), complemented by x-ray diffraction (XRD), x-ray photoemission electron microscopy (X-PEEM), and X-ray circular dichroism. We find that the low local symmetry, especially at surfaces, will split the electronic states, via spin–orbit coupling. In some cases, the result is a net spin polarization at the surface, under electric field cooling. Because of the strongly preferential surface termination of these types of materials, the boundary polarization is roughness insensitive, in some cases making spintronic device applications plausible.

3:00pm **OX+EM+HC+MI+NS+SS+TF-TuA-3 Potential Applications and Challenges for Complex Oxides in Advanced Memory and Computing Applications*, Sebastian Engelmann,*** *T Ando, V Narayanan,* IBM T.J. Watson Research Center **INVITED**

As the semiconductor industry continues to push for and develop higher performance computing systems, there is also a growing trend of redeveloping or optimizing fundamental computing approaches to be more energy efficient. The development of hardware for novel AI systems is no exception. New integration schemes, novel materials, multi-component materials or even nanoscale materials and the ability to integrate all of these approaches together becomes the compounded challenge. Deposition and etch technologies that offer differentiating solutions to these issues therefore need to meet somewhat conflicting demands, such as low damage processing as well as high rate processing beside many other issues.

Novel thin films, thin film laminates and alloys promising unprecedented performance are very interesting candidates to enable such computing paradigm shifts. In particular the class of complex oxides is a very interesting area of research as they offer new phenomena such as ferroelectricity, ferromagnetism or high temperature conductivity. While new phenomena are being discovered, unraveling the fundamental physics behind these properties is a critical element for an industrial exploitation of these properties.

In addition, these new and complex materials are growing the need for the ultimate process solution: atomic layer precision processing. Atomic layer etching is a promising path to answer the processing demands of new devices at the Angstrom scale. Self-limiting reactions, discrete reaction and activation steps or extremely low ion energy plasmas are some of the pathways being pursued for precise material removal control and maintaining the original film performance. Depending on the nature of the material, the etch response may be either too much or not enough chemical modifications of the material. Resulting modifications of the films is an important variable to consider in the readiness of material systems. In particular synergy to deposition approaches such as atomic layer deposition has been proposed as a solution, but more work is needed.

4:20pm **OX+EM+HC+MI+NS+SS+TF-TuA-7 Epitaxial Design of Complex Oxides for Catalysis and Electrocatalysis*, Yingge Du,*** Pacific Northwest National Laboratory **INVITED**

Predictive synthesis of highly active and cost-effective catalysts and electrocatalysts for energy conversion and storage is critical for leveraging intermittently available energy sources. Transition metal oxides with perovskite (ABO3) and perovskite-related structures (e.g., Brownmillerite and Ruddlesden-Popper) have been identified as robust catalysts with high oxygen reduction reaction (ORR) and/or oxygen evolution reaction (OER) activities that rival the performance of noble metals and their compounds. The study of perovskites as epitaxial thin films enables measurement of their intrinsic catalytic activity, deconvolved from the effects of surface roughness and polycrystalline defects (e.g., grain boundaries and edges between facets). In addition, epitaxial growth facilitates accurate control over the composition, crystallographic orientation, and strain in thin films.

In this talk, our recent efforts in the design of epitaxial complex oxides for catalysis and electrocatalysis will be highlighted. Using $LaNiO_3$, a bi-functional electrocatalyst, as an example, I will show how isovalent substitution, alliovalent substitution, and interfacial strain can be used to tune the structural, electronic, and optical properties of the resultant films, and how these observed changes correlate with their (electro)catalytic performance. The use of complex oxide thin films as support or anti-corrosion layers during catalytic reactions will also be discussed.

5:00pm **OX+EM+HC+MI+NS+SS+TF-TuA-9 Manipulate the Electronic Structures of Complex (Ni, Co) Oxides by Hole Doping for Oxygen Evolution Reaction*, Kelvin Zhang,*** Xiamen University, China

This talk reports a fundmanetal study on the correlation of the composition and electronic structures of complex oxides with their electrocatalytic activity for oxygen evolution reaction (OER). In particular, we modulated the electronic states of complex oxides using hole doping strategy, e.g., Li doped NiO, Sr doped $LaFeO_3$ and Ni doped Co_3O_4. Photoemission spectroscopy and x-ray absorption spectroscopy (XAS) were used to study both the occupied and unoccupied density of states around the Fermi level. The electronic structures determines the adsorption strength of reaction intermediates for OER. Our results reveal two important change in the electronic structures induced by hole doping are crucial for improving OER activity: (1) upshift of the occupied valence band center to enhance the surface absorption; (2) creation of a new hole (unoccupied) state just above the Fermi level to reduces the energy barrier for electron transfer. Our results supplemented with DFT calculations established a direct correlation between the enhancement of activity with electronic structure, providing guideline for design of highly active electrocatalysts.

5:20pm **OX+EM+HC+MI+NS+SS+TF-TuA-10 Vanadia/Tungsten Oxide on Anatase TiO2(101): a Model Catalyst Study by STM and XPS*, Tao Xu,*** *J Lauritsen, K Adamsen,* Aarhus University, Denmark*; S Wendt,* iNANO, Aarhus University, Denmark

Nitrogen oxides (NOX) from flue gas are in concern as major sources of air pollution. Increasingly stricter NOX emission control policies (e.g. Euro VI) demand innovation and better performance of NOX reduction technology. The Selective Catalytic Reduction (SCR) of NOX by vanadia supported on anatase titania, with tungsten oxide (WO3) as promoter, has been widely used for this service and attracted much research attention. However, many aspects of the SCR catalysis process remain poorly understood at the atomic level. Particularly, the synergistic effect of tungsten oxide and vanadia remain elusive in literature, despite intensive RAMAN and infrared spectroscopy studies.

In this work, we use mineral a-TiO2 single crystals exposing the (101) facets as the model surface and deposit V2O5 and WO3 in our ultrahigh vacuum chamber (UHV) chamber by e-beam evaporation in oxygen. Combining Scanning Tunneling Microscope (STM) and X-ray photon-electron Spectroscopy (XPS), we systematically investigated the morphology and oxidation state changes of the model catalyst upon heating and reactant adsorption.

The STM results illustrate the distribution of V2O5 and WO3 on anatase TiO2(101) at the atomic level. It is found that both species are highly dispersed in the sub-monolayer region. For the deposition of surface oxide species, we explored different methods to achieve the highest oxidation state of vanadium (5+) and tungsten (6+). The thermal stability of the as-deposited V2O5 and WO3 are investigated by XPS and STM systematically. We found that when V2O5 and WO3 co-exist on the a- TiO2 surface the stability of V2O5 is improved. This work provides atomic level understanding on the V2O5/WO3/TiO2 SCR catalyst and new insights into the synergistic interactions between vanadia and tungsten oxide on the a-TiO2 surface.

5:40pm **OX+EM+HC+MI+NS+SS+TF-TuA-11 Observation of Memory Effect and Fractal Surface in $SrRuO_3$ Epitaxial Thin Films*, Ratnakar Palai,*** University of Puerto Rico*; H Huhtinen,* University of Turku, Finland

Integration of multifunctional oxide materials (ferroelectrics and multiferroics) into silicon technology is of great technological and scientific interests. The current interest in functional oxides is largely based on engineered epitaxial thin films because of their superior properties compared to the bulk and polycrystalline thin films and their technological applications in dynamic random access memories, magnetic recording, spintronics, and sensors. Most of these applications require bottom and top electrodes to exploit the electronic properties of the functional materials.

SrRuO3 (SRO) has been found to be very useful for electrodes and junctions in microelectronic devices because of its good electrical and thermal conductivities, better surface stability, and high resistance to chemical corrosion, which could minimize interface electrochemical reactions, charge injection in oxide, and other detrimental processes, thus improving retention, fatigue resistance, and imprint. It also has good work function to produce the required large Schottky barrier on most ferroelectric oxide capacitors.

The bulk SRO exhibits several useful properties, such as extraordinary Hall effect, strong magnetocrystalline anisotropy, itinerant ferromagnetism, and spin-glass behavior. Spin-glass materials are currently frontier field of research and the most complex kind of condensed state of matter encountered so far in solid-state physics. Despite of the enormous importance of spin-glass models in neural networks, our knowledge of the underlying mechanistic processes involved is extremely limited. Although memory effect has been reported in bulk SRO, to our knowledge, the behavior is not well understood and there was no such report in thin films.

In this work, we report on the observation of memory effect and strong magnetic anisotropy in extremely smooth 1–3 Å roughness epitaxial (110) and (010) SrRuO3 thin films. The observation of non-zero imaginary susceptibility and frequency dependent cusp at freezing temperatures confirms the spin-glass behavior, which agrees well with the dc magnetization measurement. The origin of memory effect can be attributed to the magnetic frustration and random interaction, which is affected by dynamics of cooling and will be discussed in details.

6:00pm **OX+EM+HC+MI+NS+SS+TF-TuA-12 *In situ* Auger Electron Spectroscopy of Complex Oxide Thin Film Surfaces Grown by Pulsed Laser Deposition***, **Thomas Orvis**, M Surendran, Y Liu, A Cunniff, J Ravichandran,* University of Southern California

Complex oxides can enhance the functionality of electronic and photonic devices by supplementing them with interesting properties such as ferroelectricity, superconductivity, and magnetoresistivity. Furthermore, low dimensionality in these materials can result in additional useful properties, inspiring the continued study of complex oxides in thin film form. However, the deposition of these materials is typically governed by notoriously complex growth mechanisms, revealing the need for *in situ* probes to observe and understand their precise nature. To this end, we report the *in situ* observation of chemical composition of complex oxide thin film surfaces with Auger electron microscopy during growth by pulsed laser deposition. Our implementation of real-time monitoring techniques for complex oxide thin films sheds an important light on the intricacies of the relationships between processing conditions and resulting composition.

Plasma Science and Technology Division
Room B131 - Session PS+EM-TuA

Advanced BEOL/Interconnect Etching and Advanced Memory and Patterning

Moderators: Hisataka Hayashi, Toshiba, Japan, Kenji Maeda, Hitachi High Technologies America Inc.

2:20pm **PS+EM-TuA-1 BEOL Etch Challenges and Solutions for Advanced Process Nodes***, **Angélique Raley**, K Lutker-Lee, X Sun, Y Lu, Q Lou, N Joy, M Edley,* TEL Technology Center, America, LLC*; K Taniguchi, M Honda,* TEL Miyagi Limited, Japan*; P Biolsi,* TEL Technology Center, America, LLC **INVITED**

As logic nodes continue to scale below 7 nm, the back-end-of-line (BEOL) critical pitch has moved to sub-40 nm and is forecasted to scale down to 14 nm according to the latest International Roadmap for Devices and System (IRDS). This aggressive scaling has led to an industry wide effort in terms of materials research to manage interconnect resistance, patterning innovations to control for process variation impact and an increased focus on self-limited or highly selective processes.

In addition to the patterning and integration complexities that arise with scaling, pitch reduction has a direct impact on the plasma etch-processing window. Conventional continuous wave processes can no longer achieve stringent aspect ratio dependent etching (ARDE), selectivity and profile control requirements and have gradually given way to pulsed plasma processes, decoupled process sequence plasmas or remote plasmas to widen the process space.

In this talk, we will give an overview of plasma etching challenges and solutions for the BEOL in terms of patterning integration, dielectric etch and new materials introduction.

3:00pm **PS+EM-TuA-3 Enabling Fully Aligned Via for Advanced BEOL Nodes Scaling -Etch and Film Co-optimization***, **Xinghua Sun**, A Raley,* TEL Technology Center, America, LLC*; J Lee, J Arnold,* IBM Research Division, Albany, NY*; K Taniguchi,* TEL Miyagi Limited, Japan*; M Edley, K Lutker-Lee,* TEL Technology Center, America, LLC*; D O'Meara,* Tokyo Electron America, Inc.*; K Tapily, Y Lu, P Biolsi,* TEL Technology Center, America, LLC

Aggressive metal pitch scaling of back end of line (BEOL) interconnect for future nodes leads to increased sensitivity to via overlay and critical dimension (CD) errors, resulting in yield loss. Spacing between top and bottom metal layers in via chain macros are reaching the limits of current materials, such that device reliability may become compromised due to metal shorting or dielectric breakdown. The technique of 1-D self-aligned via (SAV) constrained by top metal hard mask (MHM) is widely used to control one direction of via CD. 2-D fully aligned via (FAV) was recently introduced to mitigate the drawbacks of SAV at via bottom. In FAV, vias are constrained with spacers resulting from recessed metal in the orthogonal direction to the MHM, thereby increasing the margin of error allowed due to CD variations and overlay shifts. However, one of the biggest challenges in successfully integration of FAV in the BEOL is maintaining the integrity of these spacers during via etch. Etch selectivity, landing on conformably deposited Nblok based cap layers, is far from sufficient to maintain good self-confinement that demonstrates adequate FAV behavior. High selectivity etch stop layers (ESL) along with compatible etches that promote soft landing on these films are required.

In this presentation, we demonstrate that etch and film can collaboratively work to make FAV a competitive solution for sub-7nm nodes. Different ESL materials and film properties are investigated in conjunction with unique via and trench etch processes to achieve optimized FAV corner shape. This work shows a multifaceted approach to successful implementation of FAV as a valuable scaling booster for advanced BEOL nodes.

3:20pm **PS+EM-TuA-4 Non-selective Silicon Oxide and Nitride Etch in Oxygen/Nitrogen-containing Fluorocarbon Plasmas***, **Yu-Hao Tsai**, D Zhang, Y Han, J Baillargeon, Y Shi, H Kim, M Wang,* TEL Technology Center, America, LLC*; T Yokoyama, M Iwata, Y Kihara, M Honda, W Sakamoto,* Tokyo Electron Miyagi Ltd., Japan*; A Mosden, A Metz, P Biolsi,* TEL Technology Center, America, LLC

Performing an all-in-one etch process for 3D-NAND fabrication requires comparable and high etch rates (E/R) for SiO_2 and Si_3N_4; the goal remains challenging. As the discrepancy of E/R largely results from the different nature of materials, surface modifications of SiO_2 and Si_3N_4 to achieve comparable composition during etch can improve the desired non-selectivity. In the presented work, we study the conversion of SiO_2 [*Submitted*] and Si_3N_4 [*J. Micro. Manuf.***1**, 20180102 (2018)] to oxynitride (SiO_xN_y) via the nitridation and oxidation-etch reactions, respectively. We computationally identify the etching mechanism of SiO_2/Si_3N_4 in the N/O-containing fluorocarbon plasmas using both quantum chemistry (QC) and molecule dynamics (MD) simulations; the surface conversion to SiO_xN_y is predicted. The results are further validated by the plasma etching of blanket SiO_2 and Si_3N_4 films in a Capacitively Coupled Plasma (CCP) chamber; both E/R trends and surface analysis on validation of oxinitride and/or nitrioxide (SiO_xN_y) formation using methods such as XPS, EDS etc. are discussed. We detail the etch reaction pathway, in which the elimination of O/N atom forming nitric oxide (NO) species is predicted. Along with that, the synergy of having F species in the process is justified. Finally, we discuss the impact of fluorocarbon to N/O ratio on the preference of either high E/R or active SiO_xN_y formation. The research builds a foundation for future development work on pursuing robust all-in-one non-selective SiO_2/Si_3N_4 etch processes.

4:20pm **PS+EM-TuA-7 Challenges in High-aspect-ratio Hole Etching for 3D Flash Memory***, **Mitsuhiro Omura**, J Hashimoto, T Adachi, Y Kondo, M Ishikawa, J Abe, I Sakai, H Hayashi,* Toshiba Memory Corporation, Japan **INVITED**

Memory devices with higher bit density are required for effective use of big data in the internet of things era, and 3D memory architecture is required. 3D flash memory encompasses numerous pillars that punch through control gate plates, and cells are arranged along the pillars [1]. We refer to each pillar as a memory hole. Memory holes are fabricated by dry etching of stacked films, which are generally constructed of dozens to several hundred pairs of SiO2/Si or SiO2/Si3N4 films. Therefore, the aspect ratio of a memory hole reaches several tens. Moreover, the critical dimension and profile of a memory hole must be strictly controlled because these features at each control gate plate directly affect the characteristics of memory cell. Therefore, the key technology of 3D flash memory is a high aspect ratio (HAR) hole etching process. However, the dry etching process of HAR holes has a variety of profile issues, including bowing, shape distortion, twisting of the hole profile, and striation.

In this study, sidewall striation formation in a HAR hole was investigated. In spite of the smooth morphology of the mask, sidewall striation was observed on dielectric films. Results from the carbon mask sample treated with several gas plasmas implies that ion irradiation can increase the degree of striation on the carbon mask, and striation tends to be suppressed by deposition of a fluorocarbon film from fluorocarbon radicals. An ion beam experiment with a simulated hole sidewall using blanket films shows that striation tends to form on the fluorocarbon film rather than on SiO2 and Si3N4 films. In connection with this result, the shallower region with striation had thicker fluorocarbon film than the deeper region with smooth sidewall. Therefore, the possible of sidewall striation formation mechanism is as follows. When the etching depth of the HAR holes reaches a certain depth, striation forms on the deposited fluorocarbon film and is transferred to the dielectric films laterally as the hole diameter increases. The region with striation depends on the aspect ratio, defined as the depth divided by the neck width of the carbon mask. Consequently, as etching progresses, the mask thickness decreases and striation forms in a deeper region, depending on the aspect ratio.

References

[1] H. Tanaka et al., Symposium on VLSI Technical Digest, 14 (2007).

5:00pm **PS+EM-TuA-9 Plasma Processing of Phase Change Materials***,* ***Ernest Chen,*** *N Altieri,* University of California, Los Angeles*; C Neumann, S Fong, H Wong,* Stanford University*; M Shen, T Lill,* Lam Research Corporation*; J Chang,* University of California, Los Angeles

The manipulation of the amorphous to crystalline phase transition observed in chalcogenide glasses for non-volatile memory applications has been studied for many years since its initial conception. However, only recently has innovation in both materials development and memory device architecture enabled phase change random access memory (PCRAM) to become a promising candidate for applications such as neuromorphic computing. Ternary chalcogenide glasses consisting of germanium, antimony, and tellurium are widely used in PCRAM applications, and Ge_2Sb-$_2Te_5$ (GST-225) will be the focus of this study.

Understanding the effects of plasma processing on the phase change material (PCM) utilized in PCRAM is crucial to ensuring proper device performance. The studies presented in this talk utilize a custom-built integrated system equipped with ion beam processing, downstream plasma processing, quadrupole mass spectrometry, optical emission spectroscopy, and x-ray photoelectron spectroscopy capabilities. The samples are prepared by sputtering from a stoichiometric GST-225 target. Prior studies have examined the behavior of GST-225 when exposed to different components of ambient exposure (N_2, O_2, and H_2O) as well as H_2 and CH_4 discharges and identified H_2 and CH_4 as capable GST etchants.

It is known that ambient exposure will cause a GST-225 layer to be oxidized in the first several nanometers, and this oxidized layer has different properties from the bulk of the GST-225 film and may also behave differently from the bulk material when exposed to plasma processing. Initial studies with *ex-situ-* XPS analysis indicate that H_2 can etch GST-225 with approximately 5% change in composition (5% increase in Ge, 5% decrease in Sb, approximately 0% change in Te) and a significant change in the ratio of 0+ to X+ (non-oxidized to oxidized) bonding states between the oxidized surface and the etched surface. In order to distinguish the effects of plasma processing on the oxidized layer and the bulk material, a custom-built downstream plasma processing chamber integrated with an XPS chamber is used. This system allows for the study of the surface states of GST-225 post-processing without any inadvertent effects from ambient conditions that may complicate *ex-situ* XPS analysis.

5:20pm **PS+EM-TuA-10 Meeting the Challenges in Patterning Phase Change Material for Next Generation Memory Devices***,* ***Meihua Shen,*** *L Thorsten, J Hoang, S Chiou, D Qian, A Routzahn, J Chen, A Dulkin, J Sims, A McKerrow, R Dylewicz,* Lam Research Corporation **INVITED**

Phase change materials (PCM) have emerged as the leading candidate for next generation non-volatile memory device with unique characteristics that significant differ from conventional DRAM and NAND flash memory. Recently, 3-D Cross point PCRAM, for example, has transitioned into high volume production, demonstrating a non-volatile memory product exhibiting faster speed, low voltage operation and high density.

Phase change materials are typically chalcogenide alloys containing elements such as Ge, Sb, Se, Te with various dopants. The materials exhibited phase change between amorphous insulating state and the crystalline conductive state under thermal/electric heating. To ensure electric device performance, it is critically important to maintaining the PCM elemental composition and structure integrity during patterning. The challenges of patterning PCM come from the soft nature of the material and the damages that can easily occur during plasma dry etch, ambient air exposure, wet clean and encapsulation process. To meet the challenges, we developed an integrated system combining dry etch, wet clean and ALD encapsulation modules together. In this paper, we will present the comprehensive studies on each module as well as the interactions of the modules in successful patterning of the phase change materials. The discussions will be focused key learnings on how to maintain the feature fidelity and the integrity of the materials during etch and encapsulation.

6:00pm **PS+EM-TuA-12 Utilizing Photosensitive Polymers to Estimate UV Radiation Exposures in Different Plasma Chamber Configurations***,* ***Luxherta Buzi,*** *M Sagianis, S Engelmann,* IBM T.J. Watson Research Center

Monitoring vacuum ultraviolet (UV/VUV) emission in plasma systems is challenging as it requires specialized diagnostic systems or sensors to be compatible with reactive ion etch (RIE) tooling. This study is mapping different reactor configurations with various levels of UV emission and its effect on a known set of polymers.

Photon-induced modifications on polymers can help decouple ion and photon effects on materials therefore, the impact of inductively coupled and microwave plasma configurations on etch rates and chemical properties of photoresists were investigated. Poly(methyl methacrylate) and Poly(4-hydroxystyrene)-based photoresists were deposited on Si wafers and exposed to argon (Ar) and nitrogen (N_2) plasmas which generate different levels of UV irradiation. X-ray Photoelectron Spectroscopy (XPS) and Fourier Transform Infrared (FTIR) were used to analyze the polymer composition and molecular structure and the surface roughness was analyzed with an atomic force microscope (AFM).

FTIR and XPS confirmed that N_2 plasma effects on chemical modifications were more pronounced on the Poly(methyl methacrylate). Roughness and etch rate was significantly higher for Poly(methyl methacrylate) compared to Poly(4-hydroxystyrene)-based photoresists. Detailed elemental and molecular structure analysis of polymers showed relatively higher damage caused from the inductively coupled plasma, which is ultimately correlated to a higher UV emission.

Materials and Processes for Quantum Information, Computing and Science Focus Topic
Room B231-232 - Session QS+2D+EM+MN+NS-TuA

Materials for Quantum Sciences

Moderators: Matthew R. Rosenberger, U.S. Naval Research Laboratory, Robert Walko, The Ohio State University

2:20pm **QS+2D+EM+MN+NS-TuA-1 Electrically Detected Electron Nuclear Double Resonance Study of Defects in 4H-SiC Bipolar Junction Transistors***,* ***Ryan Waskiewicz,*** *B Manning, D McCrory, P Lenahan,* Pennsylvania State University

There is growing interest in the possibilities of SiC in spin-based quantum computation. The development of such spin-based quantum computation will require a fundamental understanding of spin physics of paramagnetic defects in SiC including both electron and nuclear paramagnetism. We utilize electrically detected magnetic resonance (EDMR) detection through spin dependent recombination (SDR). In this study we demonstrate relatively high signal to noise electron nuclear double resonance (ENDOR) in a single fully processed SiC pn junction at room temperature. The electrically detected ENDOR (EDENDOR) involves nitrogen nuclei in close proximity to deep level centers within the depletion region of the pn junction; the deep levels are almost certainly silicon vacancies.

We believe these observations are of importance for at least two reasons: (1) they demonstrate that the enormous analytical power of ENDOR can be extended to the study of problems in conventional solid-state electronics and (2) the results demonstrate a way to directly monitor small numbers of nuclear spins through the measure of electronic currents.

In our EDMR measurements, a slowly varying magnetic field and an oscillating microwave frequency magnetic field are applied to the sample inside a microwave cavity. As in conventional EPR, energy is absorbed by paramagnetic sites when the resonance condition is met. For a simple case, this resonance condition is $hv=g\mu_B B\pm\Sigma m_i A_i$, where h is Planck’s constant, g is an orientation dependent number typically expressed in a g-tensor, $\mu_B$is the Bohr magneton, B is the magnetic field, $m_i$is the spin quantum number of the ith nucleus, and A_i is the hyperfine interaction of the ith magnetic nucleus. In EDMR, the EPR response is detected through a change in device current, in our case due to SDR.

The devices in this study are 4H-SiC BJTs. The EDMR response obtained on these BJTs is very similar to an EDMR spectrum that has been linked to a silicon vacancy in 4H-SiC MOSFETs. To perform the EDENDOR measurement, the magnetic field is held constant and an NMR frequency sweep is applied to the device. The device current is measured and a large response is measured at what is unambiguously the nuclear frequency of nitrogen. These results demonstrate the analytical power of the EDENDOR measurement, measuring nitrogen in the vicinity of the silicon vacancy defect centers that are measured with EDMR.

This work was supported by the Air Force Office of Scientific Research under award number NO. FA9550-17-1-0242.

2:40pm **QS+2D+EM+MN+NS-TuA-2 Scanning Tunneling Microscopy Studies of Er Adatoms on GaAs (110)***, **Rebekah Smith**, A Benjamin, J Gupta,* The Ohio State University

Rare earth dopants in III-V semiconductors are of interest as high quality optical sources due to the preservation of sharp intra-*f*-shell transitions. The long optical coherence lifetime and narrow energy width of these transitions, at 1.54 um, make them a candidate for quantum communication. Here we investigate Er interactions with host GaAs (110) surface with atomic resolution using STM. Er atoms were deposited via electron beam evaporation onto the GaAs surface at 5 K. We find three different Er_{ad} configurations with varying abundance upon deposition, each with a different surface site location. All three configurations exhibit long-range depressions in STM topographic images, attributed to band bending associated with a positive adatom charge state. Individual Er adatoms can be switched between these states by applying a positive voltage pulse with the STM tip. Tunneling spectroscopy on Er adsorbed at the interstitial sites reveals prominent states within the GaAs bandgap, but no evidence of sharp *f*-shell transitions inferred from bulk optical studies. We also form substitutional Er_{Ga} by applying a larger positive voltage pulse. Substitutional Er appears neutral, which we attribute to it being isoelectronic with Ga. This work acknowledges funding from the DOE (DE-SC0016379).

3:00pm **QS+2D+EM+MN+NS-TuA-3 Defect-based Quantum Systems in Hexagonal Boron Nitride***, **Trong Toan Tran**,* University of Technology Sydney, Australia **INVITED**

Engineering solid state quantum systems is amongst grand challenges in realizing integrated quantum photonic circuitry. While several 3D systems (such as diamond, silicon carbide, zinc oxide) have been thoroughly studied, solid state emitters in two dimensional (2D) materials are still in their infancy. In this talk I will introduce hexagonal boron nitride (hBN) as a promising layered material that hosts ultra bright quantum emitters. I will present several avenues to engineer these emitters in large area hBN multilayers and monolayers using chemical vapour deposition techniques. I will then show unique tuning expeirments and promising results for controlling the emission wavelength of these quantum emitters. At the second part of my talk, I will discuss promising avenues to integrate the emitters with plasmonic and photonic cavities to achieve improved collection efficiency and Purcell enhancement. These are fundamental experiments to realize integrated quantum photonics with 2D materials. I will summarize by outlning challenges and promising directions in the field of quantum emitters and nanophotonics with 2D materials and other wide band gap materials.

4:20pm **QS+2D+EM+MN+NS-TuA-7 Specific Placement of V_{Si} in 4H-SiC for Quantum Technologies using Li^+ Implantation***, S Pavunny, **Rachael L. Myers-Ward**, D Gaskill,* U.S. Naval Research Laboratory*; E Bielejec,* Sandia National Laboratories*; H Banks, A Yeats,* U.S. Naval Research Laboratory*; M DeJarld,* Raytheon*; S Carter,* U.S. Naval Research Laboratory

Silicon carbide has been a material of interest in the quantum technology field for future applications in communication and sensing due in part to the long spin (S = 3/2) coherent lifetime of the Si vacancies (V_{Si}). Additional benefits to using SiC for quantum technologies is wafer scalability and fabrication capability using standard processing techniques, making it a favorable material. To improve emission rates of photoluminescence from the vacancies, exact placement of the V_{Si} within microcavities is necessary. Here we show implanted Li^+ into Si-face, 4H-SiC homoepitaxy creates V_{Si} in desired locations. The epitaxial material had no measurable V_{Si} prior to Li^+ implantation. The dose of 100 keV L^{i+} ranged from 10^{12} – 10^{15} cm^{-2} and was directed using a maskless focused ion beam technique with a positional accuracy of ~25 nm. The arrays were characterized with high-resolution scanning confocal fluorescence microscopy. Using a 745 nm excitation source, the photoluminescence ranging from 860 – 975 nm produced the characteristic V1’, V1 and V2 lines, with the V1’ zero-phonon line being consistent for all measurements. In addition, the V1’ intensity showed a linear dependence with implantation dose. Moreover, near single photon emission is obtained from V_{Si} at the lowest doses.

Research at NRL is supported by the Office of Naval Research. Ion implantation was performed at Sandia National Laboratories through the Center for Integrated Nanotechnologies, an Office of Science facility operated for the DOE (contract DE-NA-0003525) by Sandia Corporation, a Honeywell subsidiary.

4:40pm **QS+2D+EM+MN+NS-TuA-8 Silicon Vacancy Point Defect in High-quality Nanobeam Photonic Crystal Cavities in 4H Silicon Carbide***, **Mena Gadalla**, X Zhang, A Greenspon,* Harvard University*; D Bracher,* Harvard GSAS*; R Defo, E Hu,* Harvard University

Silicon carbide (SiC) has recently found promise and applications in the quantum world, because of various fluorescent point defects that serve as an intriguing platform for solid-state quantum information and quantum sensing technologies. One such native point defect is the negatively charged silicon vacancy (V_{Si}^-)in the 4H polytype of SiC. This color center can occupy two inequivalent lattice sites, resulting in two distinct zero-phonon-lines (ZPL) at 862nm and 916nm. V_{Si}^- possesses good spin coherence properties, with spin states that can be initialized and read out optically. Unfortunately, low branching ratio is a characteristic of the V_{Si}^- spectrum where a small fraction of the total emission is coupled into the ZPL and the rest is emitted into the phonon sideband. This low emission fraction limits the ability to employ V_{Si}^- in various quantum information schemes. To increase the fraction of light emitted into the ZPL and increase the defect emission rate, we fabricated high-quality factor nanophotonic crystal cavities designed to match the ZPL frequency. Through tuning of the cavity into resonance with the ZPLs, we have demonstrated a 75-fold Purcell enhancement at 4K. This talk will describe the fabrication process for 1D nanobeam photonic crystal cavities, leading to quality factors in excess of 10^4. The highest cavity-defect interactions depend on resonance in frequency and high spatial overlap of the defect with the maximum electric field within the cavity. Using the cavity as a “nanoscope”, revealing defect position, we used laser irradiation annealing at varying times and different laser frequencies to infer the diffusive motion of defects within the cavity. We showed that a systematic and controlled laser annealing can increase the ZPL of the implanted cavity mode by a factor of 4.

5:00pm **QS+2D+EM+MN+NS-TuA-9 Tailoring the Heterogeneities in 2D Materials by Controlled Synthesis and Processing***, **Kai Xiao**, X Li, K Wang, A Oyedele, M Yoon, S Xia, M Mahjouri-Samani, C Rouleau, A Puretzky, L Liang, R Unocic, D Geohegan,* Oak Ridge National Laboratory

Two-dimensional (2D) materials are intrinsically heterogeneous, thereforecontrolling defects, understanding the impact of boundaries and interfaces and developing means to exploit these heterogeneities is a transformative opportunity that could underpin future technologies and energy applications. In this talk, I will discuss the fundamental understanding of the roles of heterogeneities including defects, dopants, edges, strain, and phases in 2D materials on their optoelectronic properties. Through isoelectronic doping in monolayer of $MoSe_2$, the Se vacancies are effectively suppressed and photoluminescence is significantly enhanced. In addition, we demonstrate the non-equilibrium, bottom-up growth approach not only can tailor the defect density far beyond intrinsic levels in monolayers of 2D $MoSe_{2-x}$but also create new antisite defects in monolayers of WS_2during the synthesis. The build-in localized strain in 2D crystals directly grown on patterned curved surface can tune the bandgap of 2D crystals for possible quantum emitting applications. The bottom up synthesis of 2D materials discussed here provides excellent control over the heterogeneity in 2D materials, which can modulate the optical and electrical properties in 2D materials and their heterostructures for ultra-thin and flexible electronics.

Acknowledgment: Synthesis science was supported by the U.S. Department of Energy, Office of Science, Basic Energy Sciences (BES), Materials Sciences and Engineering Division and characterizations were performed at the Center for Nanophase Materials Sciences, which is a DOE Office of Science User Facility.

5:20pm **QS+2D+EM+MN+NS-TuA-10 Epitaxial Al Films for Plasmonic and Quantum Computing Applications***, **Ka Ming Law**, S Budhathoki, S Ranjit, F Martin, A Hauser,* The University of Alabama

Superconducting resonators are important for application in quantum computing but require high quality factors. Much work has been done on superconducting resonators fabricated from aluminum thin films on sapphire, and superconducting Josephson tunnel junctions made from aluminum are used as the basis for quantum bit designs. In addition, epitaxial aluminum films has attracted attention in plasmonics due to their superior performance in the UV regime compared to Au and Ag, and their compatibility with current CMOS technology. Sapphire substrates are chemically stable and have low lattice mismatch with aluminum, allowing higher film quality without the need for elaborate substrate preparation and time-consuming growth procedures.

Epitaxial aluminum films were successfully grown by off-axis magnetron sputtering on c-plane sapphire. This study assessed the effects of varying both substrate preparation conditions and growth and prebake temperatures on crystallinity and smoothness. X-ray diffraction and reflectivity measurements demonstrate superior crystallinity and surface smoothness for films grown at 200℃ in15mTorr Ar. An additional substrate preparation procedure which involves 1) a modified RCA procedure and 2) prebake in oxygen environment is shown by atomic force microscopy to be highly effective in reducing void density and depth.

5:40pm **QS+2D+EM+MN+NS-TuA-11 Minimizing Coulomb Oscillation Linewidth on Silicon Quantum Dots***, **Yanxue Hong**, A Ramanayaka, M Stewart, Jr., X Wang, R Kashid, P Namboodiri, R Silver, J Pomeroy,* National Institute of Standards and Technology (NIST)

In quantum science research, both cryogenic temperatures and low measurement noise are required for high fidelity. For silicon quantum dot devices, an increase in either one causes broadening of Coulomb blockade peaks, which is usually referred to as a high electron temperature. Here we report on temperature-dependent (T-dependent) conductance measurements and evaluation of effective electron temperature (T_{eff}) using an STM-patterned atom-scale silicon single-electron transistor (SET). Measurements are made in various cryogenic systems over temperatures varying from 10 mK to 25 K. The effective electron temperature is extracted by fitting the experimental data using a theoretical model. We initially find that the measured peak width has a linear dependence on the bath temperature above 1 K and saturates below 1 K. In addition, a considerable mismatch (> 2 K) between the lattice (thermometer) temperature and the carrier temperature (T_{eff}) is observed. Therefore, the Coulomb resonance is not only thermally broadened by T_{eff} but also broadened by other T-independent sources such as gate noise, triboelectric noise, etc. We study the origins of the saturation at low temperature regime and analyze factors inducing high T_{eff}. We report on progress to reduce the noise and reach an effective temperature of < 300 mK. Since our silicon SETs have high charging energies and large energy level spacings, we also seek to measure the transition from classical (multilevel) regime to quantum (single-level) regime by manipulating the bath temperature.

6:00pm **QS+2D+EM+MN+NS-TuA-12 Micro-magnetic Simulations of Correlated Switching in Touching Nano-magnetic Elements***, **Tejumade Durowade**, V Metlushko,* University of Illinois at Chicago

Nanomagnets hold significant potential for use as building blocks for room temperature quantum computers. Bistability based on stable ground magnetization states means power dissipation can be extremely low and their small size allows magnetization to be maintained for a long period time [1]. With packing density on the order of 10^{10} /cm^2 and switching frequency in the terahertz range, nanomagnets are a promising replacement for current state of art metal oxide semiconductor processes that are already at the limits of continued scaling. In this work, we present the results of simulations of touching nanomagnetic disks that can be used for room operable quantum computing. Like gears in a mechanical system, the chirality of the magnetization in each disk is determined through interaction with its neighbors. These simulations offer insight into the switching dynamics within the disks as current experimental techniques lack the combined temporal and spatial resolution needed to observe the formation and annihilation of the magnetic domains that facilitate the switching process. The switching of touching symmetric disks can be achieved at zero applied field as the disks settle into a remanent vortex state, meaning minimal energy loss during the process. Due to the quantum exchange force, at the point of contact between disks, the magnetization vectors rotate in the same direction giving rise to opposite chiralities in the disks. Since logic states can be represented using the chirality of the in-plane magnetization, configurations of touching disks can potentially be used to implement basic or complex logic functions. Maintaining coherence of opposite chirality in chains of disks was achieved with the introduction of a biasing element to eliminate the bidirectionality of interaction between disks.

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2D Materials
Room A226 - Session 2D+EM+MI+MN+NS+QS-WeM

Novel 2D Materials

Moderator: Phil King, University of St Andrews

8:00am **2D+EM+MI+MN+NS+QS-WeM-1 A Safari Through Thousands of Layered Materials Guided by Data Science Techniques***, **Evan Reed**, G Cheon,* Stanford University **INVITED**

We have utilized data mining approaches to elucidate over 1000 2D materials and several hundred 3D materials consisting of van der Waals bonded 1D subcomponents, or molecular wires. We find that hundreds of these 2D materials have the potential to exhibit observable piezoelectric effects, representing a new class of piezoelectrics. A further class of layered materials consists of naturally occurring vertical hetero structures, i.e. . bulk crystals that consist of stacks of chemically dissimilar van der Waals bonded layers like a 2-D super lattice. We further combine this data set with physics-based machine learning to discover the chemical composition of an additional 1000 materials that are likely to exhibit layered and two-dimensional phases but have yet to be synthesized. This includes two materials our calculations indicate can exist in distinct structures with different band gaps, expanding the short list of two-dimensional phase change materials. We find our model performs five times better than practitioners in the field at identifying layered materials and is comparable or better than professional solid-state chemists. Finally, we find that semi-supervised learning can offer benefits for materials design where labels for some of the materials are unknown.

8:40am **2D+EM+MI+MN+NS+QS-WeM-3 2D Ferroelectric Semiconductor α-In_2Se_3 for Non-Volatile Memory Applications***, M Si, **Peide Ye**,* Purdue University

α-In_2Se_3 is a novel two-dimensional (2D) ferroelectric semiconductor. It has a bandgap of ~1.39 eV, room temperature ferroelectricity, the ability to maintain ferroelectricity down to a few atomic layers and the feasibility for large-area growth. Based on the ferroelectric and semiconducting nature of the material, a ferroelectric semiconductor field-effect transistor (FeS-FET) was proposed and experimentally demonstrated [1]. In the FeS-FET, a ferroelectric semiconductor is employed as the channel material while the gate insulator is the dielectric. The two non-volatile polarization states in FeS-FETs exist in the ferroelectric semiconductor channel. Therefore, a high quality amorphous gate insulator can be used instead of the common polycrystalline ferroelectric insulator for Fe-FETs. The fabricated FeS-FETs exhibit high performance with a large memory window, a high on/off ratio over 10^8, a maximum on-current of 862 μA/μm, low supply voltage with scaled gate insulator and the potential to exceed the existing Fe-FETs for non-volatile memory applications.

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9:00am **2D+EM+MI+MN+NS+QS-WeM-4 *Ab initio* Informed Theory of Axis-dependent Conduction Polarity in Goniopolar Materials***, **Yaxian Wang**, B He, M Arguilla, N Cultrara, M Scudder, J Goldberger, J Heremans, W Windl,* The Ohio State University

$NaSn_2As_2$ has recently been synthesized and was found to be an exfoliatable van der Waals Zintl phase, opening new opportunities for electronic design on the few-atom-thick scale. Although the band structure may suggest a range of metal to semi-metal, it shows strong anisotropy especially in its "polarity", characterized by its dominant carrier type, which strongly affects its electronic and thermal properties. We used DFT calculations to investigate bandstructure and Fermi surface. In addition, we employed BoltzTraP code to calculate the transport behavior in in/cross-plane directions, predicting strongly anisotropic carrier transport and directionally dependent polarity –"goniopolarity" – in this layered material. It is confirmed by experimental thermopower measurements. We show from simulations on a model band structure the Fermi surface geometry origin in a single-band toy model, and we utilize the bandwidth concept from a tight-binding model to give an insight of real space orbital contributions and nature of the bonding states in this layered crystal. Based on that, additional candidate materials for goniopolarity can be proposed, and the design space for goniopolar materials in general will be defined.

9:20am **2D+EM+MI+MN+NS+QS-WeM-5 In-Plane Mechanical Properties and Strain Engineering of 2D Hybrid Organic-Inorganic Perovskites***, **Qing Tu**, I Spanopoulos, S Hao, C Wolverton, M Kanatzidis, G Shekhawat, V Dravid,* Northwestern University

Two-dimensional (2D) hybrid organic-inorganic perovskites (HOIPs) are new members of the 2D materials family with wide tunability, highly dynamic structural features and excellent physical properties. Mechanical strain is inevitable in 2D-HOIP-based applications due to materials processing, thermal expansion and substrate deformation. Understanding the mechanical properties and strain engineering of such functional materials are both fundamentally and practically important to achieve high performance and mechanically stable (flexible) devices. Here the in-plane mechanical properties and the impact of in-plane uniaxial tensile strain on the electronic properties of 2D lead iodide perovskites with a general formula $(CH_3(CH_2)_3NH_3)_2(CH_3\text{-}NH_3)_{n-1}Pb_nI_{3n+1}$ were reported for the first time. The in-plane Young's modulus and breaking strength of ultrathin 2D HOIP flakes were measured by AFM-based nanoindentation of suspended 2D HOIP membranes.[1] The in-plane Young's moduli of 2D HOIPs are smaller than that of conventional covalently bonded 2D materials like graphene and MoS_2 due to the much more deformable $[PbI_6]^{4-}$ octahedra structure. Both the Young's modulus and breaking strength first decrease and then plateau as the thickness of 2D HOIP flake increases from monolayer to 4 layers, which is attributed to interlayer slippage during deformation. Ultrathin 2D HOIPs exhibit outstanding breaking strength/Young's Modulus ratio compared to many other widely used engineering materials and polymeric flexible substrates, which renders them suitable for application into flexible electronic devices. Furthermore, the uniaxial tensile strain was found to increase the band gap of 2D HOIPs.[2] Such strain effect on the band gap of 2D HOIPs is fully reversible and depends on the structural unit of the materials. For2D HOIP with n = 5, the strain response of the band gap can be as high as 13.3 meV/%. First-principles simulations show that the strain response of the band gap arises from the rotation of the inorganic $[PbI_6]^{4-}$ octahedra and the consequential Pb-I bond stretching and increase of Pb-I-Pb angle. The observed band gap–strain relationship can be harnessed to map the local mechanical strain in 2D HOIP-based devices and allow 2D HOIPs for sensing applications.

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9:40am **2D+EM+MI+MN+NS+QS-WeM-6 Collective Electronic States of Epitaxial Monolayer 1T-$NbSe_2$***, **Zhuozhi Ge**,* University of Wisconsin*; H Zhang, L Liu, C Yan,* West Virginia University*; M Weinert,* University of Wisconsin*; L Li,* West Virginia University

At the single layer limit, transition metal dichalcogenides (TMDs) can adopt two different structural variants depending on the anionic environment around the metal ions: the anions are arranged in trigonal prismatic fashion in the 1H polymorph, whereas in 1T the arrangement is octahedral. While bulk 1T $NbSe_2$ doesn't exist in nature, here we show that single layer 1T $NbSe_2$ polymorph can be grown by molecular beam epitaxy on epitaxial graphene/SiC(0001) substrates. A (Ö13xÖ13) Star-of-David charge density waves is observed by *in situ* scanning tunnelling microscopy, which persists above room temperature. A gap of 0.50 eV is further observed by tunnelling spectroscopy and angle resolved photoemission spectroscopy, indicating that this monolayer 1T phase of $NbSe_2$ is also a Mott insulator, similar to that of bulk 1T TaS_2. Our findings indicate that the presence of epitaxial constraints can generate structural configurations that are prohibited in fully-bonded TMD crystals. These findings and their implication on the collective electronic states of single layer 1T-$NbSe_2$ will be discussed at the meeting.

11:00am **2D+EM+MI+MN+NS+QS-WeM-10 Magnetic Interfaces of MnSe2 Monolayer***, **Tomas Rojas**, S Ulloa,* Ohio University

Until recently, 2D magnetism was thought to occur together with defects or doping on different substrates. This situation changed drastically, as intrinsic Cr-based ferromagnetic monolayer materials were discovered, namely CrI3 and Cr2Ge2Te6. A different material, MnSe2, was predicted as stable ferromagnetic monolayer by first-principles calculations, and it has been successfully grown on several substrates. In this study, the authors confirm the intrinsic ferromagnetism of the monolayer, while for thicker samples they report an interface of the MnSe2 monolayer with bulk α-MnSe(111). This phase of the material is non-magnetic, and yet the observed magnetic moments are of up to twice the value of those in the monolayer alone. In this work, we present a detailed analysis of the interactions at this interface between the two phases, using the Heyd-Scuseria-Ernzerhof hybrid functional. We have studied the effects on the electronic and magnetic structure of both phases of the material, and the dependence on the sample thickness. We study the role that strain plays at the interface, and how it affects the magnetic moments of the structure.

Supported by NSF-DMR 1508325, and Ohio Supercomputer Center .

11:20am **2D+EM+MI+MN+NS+QS-WeM-11 Orbital Design of Topological Insulators from Two-dimensional Semiconductors***, **Shixuan Du**,* Institute of Physics, Chinese Academy of Sciences, China

Two-dimensional (2D) materials have attracted much recent attention because they exhibit various distinct intrinsic properties/functionalities, which are, however, usually not interchangeable. Interestingly, here we propose a generic approach to convert 2D semiconductors, which are amply abundant, to 2D topological insulators (TIs), which are less available, via selective atomic adsorption and strain engineering. The approach is underlined by an orbital design principle that involves introducing an extrinsic -orbital state into the intrinsic -bands of a 2D semiconductor, so as to induce - band inversion for a TI phase, as demonstrated by tight-binding model analyses. Remarkably, based on first-principles calculations, we apply this approach to convert the semiconducting monolayer CuS and CuTe into a TI by adsorbing Na and K respectively with a proper -level energy, and CuSe into a TI by adsorbing a mixture of Na and K with a tuned -level energy or by adsorbing either Na or K on a strained CuSe with a tuned -level valence band edge. Our findings open a new door to the discovery of TIs by a predictive materials design, beyond finding a preexisting 2D TI.

This work is in collaboration with Lei Gao and Jia-Tao Sun from IoP-CAS, Gurjyot Sethi and Feng Liu from University of Utah, Yu-Yang Zhang from UCAS.

11:40am **2D+EM+MI+MN+NS+QS-WeM-12 Rotationally Controlled van der Waals Heterostructures of 2D Materials***, **Emanuel Tutuc**, K Kim, G Burg, H Movva,* The University of Texas at Austin **INVITED**

Heterostructures of atomic layers such as graphene, hexagonal boron-nitride, and transition metal dichalcogenides (TMDs) can serve as testbed for novel quantum phenomena in two-dimensions, and potential device applications. A key ingredient that can add a new dimension to the atomic layer heterostructures palette is the rotational control, and alignment of different two-dimensional (2D) layers. We review here an experimental technique that enables rotationally controlled heterostructures with accurate alignment of the individual layer crystal axes [1]. We illustrate the applicability of this technique to the rotationally aligned double layers of graphene [2], or TMDs [3] separated by a tunnel barrier which display resonant, energy- and momentum-conserving tunneling in vertical transport, consistent with theoretical expectations. When two 2D layers are overlaid with a relative twist, the resulting heterostructure shows a new type of periodicity associated with the moiré superlattice, which are only beginning to be systematically investigated as platform for strongly correlated electron physics. We discuss the electron transport in tunable moiré patterns realized in twisted bilayer [4], and double bilayer graphene heterostructures.

Work done in collaboration with S. K. Banerjee, L. F, Register, B. J. LeRoy, A. H. MacDonald, T. Taniguchi, and K. Watanabe.

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Spectroscopic Ellipsometry Focus Topic
Room A212 - Session EL+AS+EM+TF-WeM

Optical Characterization of Thin Films and Nanostructures

Moderators: Eva Bittrich, Leibniz Institute of Polymer Research Dresden, Tino Hofmann, University of North Carolina at Charlotte

8:00am **EL+AS+EM+TF-WeM-1 Enhanced Strong Near Band Edge Emission from Lanththanide Doped Sputter Deposited ZnO***, C Heng,* Beijing Institutute of Technology, China*; W Xiang, T Wang,* Beijing Institutete of Technology, China*; W Su,* Beijing Instititute of Technology, China*; P Yin,* Beihang University, China*; **Terje G Finstad**,* University of Oslo, Norway

Research on ZnO films and nanostructures have increased steadily in the last decades being motivated by many applications including photonic applications. Incorporation of rare earth (RE) elements for the purpose utilize transition therein for conversion or manipulation of the wavelength spectrum. That was also our original motivation, however we observed the REs also can provide an enhancement of near band gap emission,NBE. This has been observed for Tb, Ce, Yb and Eu. The ZnO films were co-sputtered with RE elements onto Si wafers in an Ar+O_2 ambient yielding oxygen rich films as observed by RBS and XPS. The films were annealed in an N_2 ambient for various temperatures from 600 to 1100 °C. The luminescence behavior was studied emission and excitation spectroscopy as well luminescence decay measurements. Both undoped and RE doped films showed a large increase in emission with increasing annealing temperature, while the increase was largest for the RE doped samples. The crystallinity and microstructure of the films were studied by XPS, SEM, XRD and HRTEM. It is observed that the increase in UV NBE is correlated with crystalline improvements of ZnO. At the temperature for maximum PL emission intensity there is silicate formation due to interaction with the substrate. The maximum occurs for an annealing temperature where not all the ZnO has been consumed in the silicate reaction. This maximum appears to be 1100 °C for the thicker films and 1000 °C for thinner films. For samples having maximum NBE there seem to be random lasing occurring indicated by the intensity dependence of UV PL emission. A hypothesis for the main reason behind the increase in NBE intensity with RE doping is that the RE ions influence the film structure during nucleation early in the deposition process by influencing the mobility of atoms. The initial grain structure will have an affect on the development grain structure for the whole film and an influence on the grain growth. This influences the presence of non-radiative defect centers in the film and the grain surface and grain boundaries. As a side effect, we observe that there is very little transfer of excitation energy to the RE ions. This supports the notion that oxygen deficient centers may be necessary to have efficient energy transfer to RE ions in ZnO. Finally we remark that strong UV light from ZnO films have been sought particularly because they could offer a low temperature production for some application. The present method is still a high temperature method, but it is very simple and can be directly combined with Si technology which can be advantage for certain applications.

8:20am **EL+AS+EM+TF-WeM-2 Ellipsometry Study of PLD based Temperature Controlled Thin Film Depositions of CdSe on ITO Substrates***, **Flavia Inbanathan**,* Ohio University*; M Ebdah,* King Saud University, Kingdom of Saudi Arabia*; P Kumar,* Gurukula Kangri Vishwavidyalaya, India*; K Dasari,* Texas State University*; R Katiyar,* University of Puerto Rico*; W Jadwisienczak,* Ohio University

Cadmium Selenide(CdSe), a n-type semiconductor with a direct bandgap of 1.73eV has been explored widely for its suitability in various applications including photovoltaics and optoelectronics, because of its optical and electrical properties. The literature presents various deposition methods for CdSe thin films out of which this work is based on pulsed laser deposition(PLD)[1]. The optoelectronic applications of CdSe thin films depend on their structural and electronic properties that depends on deposition and process parameters[2]. The stability of the thin films at various temperatures is an important factor to improve the efficiency and durability of photosensitive devices. The present work aims to fabricate the high quality CdSe thin films using PLD method and affirms the optimal deposition temperature at 250°C as validated by the films surface roughness and ellipsometry studies[3][4]. The effect of different *in-situ* deposition temperature on structural, morphological and optical properties through XRD, AFM, SEM, optical absorption/transmission and ellipsometry spectroscopy have been investigated. CdSe thin films with thickness close to 200nm were deposited on the Indium Tin Oxide (ITO) coated glass substrates at temperatures ranging from 150 to 400°C. The light absorption spectrum analysis of all the CdSe films confirmed well defined direct energy band gap from 2.03 to 1.83eV. The ITO substrate is modelled using a two sub-layers model that consists of 130nm graded ITO on top of a 0.7mm bulk ITO layer, and the experimental ellipsometry spectra agreed very well with the fitting spectra. The ellipsometry study confirmed that CdSe thin films show an increase of 44% in refractive index(*n*) in the violet spectrum, and a constant value in blue-yellow spectral range but with significant changes in red spectrum for increase in temperature upto 350°C; beyond which resulted in constant value, possibly due to the stagnation in the grain growth. The extinction coefficient(*k*) value of CdSe approaches zero in the red spectrum region for 150^{o}C and 300^{o}C temperatures whereas it showed a value of 0.25 and 0.7 for 250^{o}C and 400^{o}C temperatures, respectively. The peaks observed around 650nm and 750nm in ellipsometry spectra are assigned to excitonic transitions. The collected data will be critically analysed in terms of CdSe optical properties engineered for optoelectronic and photovoltaic applications.

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8:40am **EL+AS+EM+TF-WeM-3 The Application of Mueller Matrix Spectroscopic Ellipsometry to Scatterometry Measurement of Feature Dimension and Shape for Integrated Circuit Structures***, **Alain C. Diebold,*** SUNY Polytechnic Institute **INVITED**

One of the most difficult measurement challenges is non-destructively determining the feature dimensions and shape for complicated 3D structures. This presentation will review Mueller Matrix Spectroscopic Ellipsometry based scatterometry which uses the Rigorous Coupled Wave Approximation (RCWA) to solve Maxwell's equations for a model structure and the resulting Mueller Matrix elements are compared to experimental results. Here we use the structures used in GAA transistors fabrication as an example of challenging measurements.(1, 2, 3) In this talk, we present simulations aimed at understanding the sensitivity to changes in feature shape and dimension for the structures used to fabricate GAA transistors. Simulations of the multi-layer fins show a clear sensitivity to fin shape and Si layer thickness which is enhanced by the use of the full Mueller Matrix capability vs traditional spectroscopic ellipsometry. We also discuss experimental measurement of nanowire test structure demonstrating the ability to measure the etching of mutiple sub-surface features. [3]

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9:20am **EL+AS+EM+TF-WeM-5 Optical Constants and Thickness of Ultrathin Thermally Evaporated Iron Films***, **Nick Allen**, D Shah, R Vanfleet, M Linford, R Davis,* Brigham Young University

Carbon nanotube templated microfabrication (CNT-M) is a technique that uses a patterned iron catalyst to grow 3-D structures for device applications. Iron catalyst thickness strongly affects carbon nanotube (CNT) growth heights and the straightness of the CNT-M structures. Atomic force microscopy has been used to directly measure the thicknesses of such iron/iron oxide films, but this technique is slow and not easily scalable. A faster method is ellipsometry, but for very thin films, the optical constants and thickness are not easily separated, thus standard ellipsometry approaches are inadequate. The 2-6 nm thick iron films used as CNT growth catalysts are in this challenging region. The absorptive nature of the iron/iron oxide films adds further difficulty. In this study, a multi-sample ellipsometry analysis using iron films of various thicknesses was performed to obtain the optical constants of thermally evaporated iron. We used contrast enhancement by incorporating a silicon dioxide layer under the film being analyzed to enhance sensitivity to the optical constants.

9:40am **EL+AS+EM+TF-WeM-6 Birefringent Photonic Crystals for Polarization-discriminatingInfrared Focal Plane Arrays***, **Marc Lata**, Y Li, S Park, M McLamb, T Hofmann,* University of North Carolina at Charlotte

Infrared optical materials fabricated using direct laser writing have received substantial interest since the emergence

of this technology which is based on the two-photon polymerization of suitable monomers [1, 2]. We have

demonstrated that direct laser writing allows the fabrication of structured surfaces to reduce Fresnel reflection

loss in the infrared spectral range while two-dimensional photonic crystals enable optical filters with high spectral

contrast [3, 4]. In combination with the ability to fabricate large scale arrays of uniform structures, two-photon

polymerization could be a disruptive technology for enhancing focal plane arrays in IR imaging systems.

So far, photonic crystals which provide polarization selectivity have not been used for the pixel-based enhancement

of infrared focal plane arrays. Here we explore the form-birefringence found in photonic crystals composed

of arrays of subwavelength-sized slanted micro wires (Fig. 1) for this purpose. The photonic crystals investigated

here were fabricated in a single fabrication step using direct laser writing of an infrared transparent photoresist.

The lateral dimensions of the photonic crystals are comparable to the pixel size of infrared focal plane arrays which

is on the order of some tens of micrometers [5]. We observe a strong contrast under cross-polarized illumination

in the mid-infrared spectral range at w = 1550 cm-1. Finite-element-based techniques are used to optimized the

geometry of the constituents of the photonic crystals to minimize edge effects. We envision laser direct writing as

a suitable technique for the enhancement of focal plane arrays to enable focal-plane polarimeters for the infrared

spectral range.

11:00am **EL+AS+EM+TF-WeM-10 Relevance of hidden Valleys in the Dequenching of Room-temperature-emitting Ge Layers***, T Sakamoto, Y Yasutake,* University of Tokyo, Japan*; J Kanasaki,* Osaka City University, Japan*; **Susumu Fukatsu**,* University of Tokyo, Japan

Ge offers a unique advantage of gaining a deeper insight into the intervalley coupling of *hot* electrons [1], which is arguably of importance in the context of controlling the optoelectronic and photonic functionalities [2]. In view of the complicated valley degeneracy in the near-band-edge region, such intervalley coupling of electrons plays a pivotal part even when strain-engineering pseudomorphic Ge-based quantum structures.

The capability of direct-gap emission at room temperature is of considerable practical significance of Ge, for which an added advantage is that emission wavelengths fortuitously fall within the telecom bands. Moreover, Ge is particularly interesting from the device physics point of view as it outperforms many semiconductor allies in the sense that thermal *dequenching* occurs near room-temperature: the emitted light intensity increases with increasing temperature, which is convenient but nevertheless logic-defying.

Such a rather counterintuitive "thermal roll-up", as opposed to thermal roll-off which is usually more relevant, has been interpreted in terms of two-level electron kinetics assuming local thermal equilibrium; long-lived electrons populating the indirect conduction-band bottom, i.e., L-valleys, are excited up into the direct-gap Γ-valley by absorbing phonons, which seems to fit a fairly standard phenomenological picture reasonably well. To the contrary, this model system fails in the case of Ge layers, the quality of crystallinity of which is compromised because of a low growth temperature. In fact, they only show steady thermal roll-off, viz. *quenching*, without a trace of the anticipated dequenching.

These apparently conflicting observations can be reconciled only by considering another otherwise invisible *hidden* conduction-band valley that comes in between the L andΓ valleys to decouple them. A three-level scheme is naturally invoked thereby. Indeed, it explains not only the missing dequenching but the lost local thermal equilibrium in low-quality layers. As a proof of such a conjecture, an attempt was made to directly capture the *hidden* valleys by means of time- and angle-resolved two-photon photoemission [3]. Preliminary results indicate the relevance of X(Δ)-valleys, which are slightly above the Γ-valley, in the dequenching of room-temperature emission as a result of ultrafast coupling of L-X(Δ)-Γ valleys by phonons taking up large crystal momenta. These are consistent with theory and luminescence study.

1. T. Sakamoto *et al.*, Appl. Phys. Lett. **105**, 042101 (2014).

2. Y. Yasutake and S. Fukatsu, Spoken at 2018 APS March Meeting (Los Angeles, 2018), P07.00012.

3. J . Kanasaki *et al.*, Phys. Rev. B **96**, 115301 (2017).

11:20am **EL+AS+EM+TF-WeM-11 Spectroscopic Ellipsometry on Organic Thin Films - From in-situ Bio-sensing to Active Layers for Organic Solar Cells***, **Eva Bittrich**, P Uhlmann, K Eichhorn,* Leibniz Institute of Polymer Research Dresden, Germany*; M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany*; M Levichkova, K Walzer,* Heliatek GmbH, Germany **INVITED**

Nanostructured surfaces and thin films of small organic molecules, polymers or hybrid materials are promising interfaces for versatile applications like sensing, water purification, nanoelectronics, energy production and energy storage devices. Ellipsometry, as non-invasive method, is well suited to contribute to the understanding of structure – property – relationships in organic thin films, but can also act as probing technique for hybrid sensing elements. Aspects from our research ranging from switchable responsive polymer brush interfaces for biosensing to thin films of small organic molecules for organic solar cells will be presented. On the one hand, swelling of polymer brushes grafted to slanted columnar thin films of silicon will be visualized by anisotropic optical contrast microscopy, as an example for a new class of hybrid sensing materials with unique sensitivity on the nanoscale. On the other hand the effect of template molecules on the morphology and optical properties of semiconducting thin films will be discussed, emphasizing the correlation of ellipsometric data with structural analysis by grazing incidence wide angle X-ray scattering (GIWAXS).

12:00pm **EL+AS+EM+TF-WeM-13 Optical Dielectric Function of Si(bzimpy)2 – A Hexacoordinate Silicon Pincer Complex Determined by Spectroscopic Ellipsometry***, **Yanzeng Li**, M Kocherga, S Park, M Lata, M McLamb, G Boreman, T Schmedake, T Hofmann,* University of North Carolina at Charlotte

Tang and VanSlyke demonstrated light emission from the first practical electroluminescent device based on a double-organic-layer structure of tris(8-hydroxyquinoline)aluminum, Alq_3, and a diamine film in the late 80's. Since then, organic light emitting diodes (OLED) based on metal chelates such as Alq3 have been widely studied. Despite the widespread use of Alq_3, there has been a broad search for new materials with improved properties, in particular, with respect to their chemical and electrochemical stability. We have recently reported on the successful synthesis of a neutral, hexacoordinate silicon-based fluorescent complex $Si(bzimpy)_2$. Our results indicate that $Si(bzimpy)_2$ exhibits inherent advantages such as the tunability of the luminescence in the visible spectrum, greater thermal stability, and high charge mobility that is comparable to that of Alq_3. Despite the successful synthesis and encouraging electroluminescence at 560 nm the complex dielectric function of the water stable complex has not been reported yet. Here we present spectroscopic ellipsometry data which were obtained from a Si(bzimpy)2 thin-film in the spectral range from 300~nm to 1900~nm. A parameterized model dielectric function composed of a Tauc-Lorentz and Gaussian oscillators is employed to analyze the experimental ellipsometry data. We find a good agreement between the critical point energies observed experimentally and our density functional theory calculations reported recently.

Electronic Materials and Photonics Division
Room A214 - Session EM+2D+AS+MI+MN+NS+TF-WeM

Nanostructures and Nanocharacterization of Electronic and Photonic Devices

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

8:00am **EM+2D+AS+MI+MN+NS+TF-WeM-1 Photonic Thermal Conduction in Semiconductor Nanowires***, E Tervo, M Gustafson, Z Zhang, B Cola, **Michael A. Filler**,* Georgia Institute of Technology

We present a practical material system—chains of infrared plasmonic resonators situated along the length of semiconductor nanowires—where near-field electromagnetic coupling between neighboring resonators enables photonic thermal transport comparable to the electronic and phononic contributions. We model the thermal conductivity of Si and InAs nanowires as a function of nanowire diameter, resonator length, aspect ratio, and separation distance by combining discrete dipolar approximation calculations, to determine the relevant dispersion relations, with thermal kinetic theory. We show that photonic thermal conductivities exceeding 1 $W\ m^{-1}\ K^{-1}$ are possible for 10 nm diameter Si and InAs nanowires containing repeated resonators at 500 K, more than an order of magnitude higher than existing materials systems and on par with that possible with phonons and electrons. These results highlight the potential for photons in properly engineered solids to carry significant quantities of heat and suggest new ways to dynamic control thermal conductivity.

8:20am **EM+2D+AS+MI+MN+NS+TF-WeM-2 Electric Field-Induced Defect Migration and Dielectric Breakdown in ZnO Nanowires***, **Hantian Gao**, M Haseman,* Department of Physics, The Ohio State University*; H von Wenckstern, M Grundmann,* Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik*; L Brillson,* The Ohio State University

Nanowires of the II-VI compound semiconductor ZnO have generated considerable interest for next generation opto- and microelectronics . Central to nanowire electronics is understanding and controlling native point defects, which can move[1] and lead to dielectric breakdown under applied electric fields. We used nanoscale lateral and depth-resolved cathodoluminescence spectroscopy (DRCLS) with hyperspectral imaging (HSI) in a scanning electron microscope (SEM) to observe defect migration and redistribution directly under applied electric fields and after dielectric breakdown. HSI maps represent lateral intensity distributions of specific features acquired pixel by pixel across SEM-scanned areas and normalized to near band edge (NBE) emissions. A pulsed layer deposited (PLD) ZnO microwire (3 µm diameter) exhibited homogeneous distributions of common luminescence features at 2.0 eV (V_{Zn} cluster) and 2.35 eV (Cu_{Zn}) as well as 2.7 and 2.9 eV (V_{Zn}) peaks near the wire surface. With increasing electrical bias up to $3x10^5$ V/cm between two Pt contacts, these defects systematically redistribute, even at room temperature, moving toward and under one of the contacts, draining the “bulk” nanowire, especially its near-surface region. Since ionized V_{Zn}-related and Cu_{Zn} antisite defects are acceptors, their removal reduces the compensation of electron density in the typically n-type ZnO and thus its resistivity.

Besides HSI lateral maps, DRCLS vs. incident beam energy yields depth profiles radially of defects at specific locations along the nanowire. These exhibit high near-surface and wire core densities that biasing reduces. Current voltage measurements with increasing field gradients show a gradual resistivity decrease until an abrupt dielectric breakdown of the microwire at 300 kV/cm (150 V/5 µm). The acceptor removal between the contacts and their accumulation under one of the contacts can both contribute to this breakdown due to the decrease in resistivity and higher current conduction between the contacts and possible defect-assisted tunneling[2] across the increased defect density under the contact, respectively. These electric field-induced defect movements may be of more general significance in understanding dielectric breakdown mechanism not only in ZnO nanostructures but also bulk semiconductors in general.

HG, MH, and LJB gratefully acknowledge support from AFOSR Grant No. FA9550-18-1-0066 (A. Sayir). HVW and MG acknowledge Deutsche Forschungsgemeinschaft (Gr 1011/26- 1).

1. G. M. Foster, et al., Appl. Phys. Lett. **111**, 101604 (2017).

2. J.W.Cox, et al., Nano Lett, **18**, 6974 (2018).

8:40am **EM+2D+AS+MI+MN+NS+TF-WeM-3 Characterization of SiGe/Si Multilayer FIN Structures using X-Ray Diffraction Reciprocal Space Maps***,*

Roopa Gowda*, M Korde,* SUNY Polytechnic Institute*; M Wormington,* Jordan Valley Semiconductors Inc.*; A Diebold,* SUNY Polytechnic Institute

Nanowire and Nanosheet FET's are potential replacements for FinFET's, mainly beyond sub-10nm CMOS technology nodes, as gate-all-around (GAA) FET device architecture provides improved electrostatics in higher on current (*I* on) and better subthreshold swing. As GAA is one of the best promising device for logic applications for future technology nodes, there is an increased need of characterization technique for such multilayer $Si_{1-x}Ge_x$/ Si complex structures. We studied $Si_{1-x}Ge_x$/Si/Si_{1-}xGex/Si/$Si_{1-x}Ge_x$/Simultilayer FIN structures using X-Ray Diffraction Reciprocal Space Maps (RSM). RSM is one of the most popular technique to study epitaxial thin-films nanostructures due to straightforward analysis of the data. We found RSM simulations showing sensitivity of nanosheet fin structures dimensions such as pitch-walk (PW), Nanosheet thickness (NST), composition and shape. RSM's provide better means to interpret more complex diffraction measurements than real space constructions. RSMs of $Si_{1-x}Ge_x$/Si multilayer structure has been simulated using Bruker JV-RADS v6.5.50/HRXRD software. 1D line profiles extracted from RSMs was also used for the analysis of nanostructures dimensions. We obtained multilayer structure dimensions from the published information. We studied the influence of nanostructure parameters PW, NST, Composition and shape on RSMs. Imperfect periodic structures impact the intensity modulation of the grating rods (GRs). We observed that satellite peaks intensity reduces and harmonics peaks intensity enhances as PW increases. Rate of intensity change in higher order peaks is much faster than the lower harmonic peaks. We observed that the spacing between adjacent interference fringes in RSMs is related to the thickness of the layers. The period of fringes is inversely proportional to the thickness of the layer, hence total FIN height can be determined. 1D line profiles along Q_z shows decreased angular width and increase in intensity of the layer peak and interference fringes as NST increases. Symmetric 004 longitudinal RSMs and their line profiles clearly show layer peak shift from substrate peak as composition increases due to increase of SiGe lattice spacing along the growth direction. Cross-shaped GR pattern in RSMs is observed which is due to trapezoidal surface grating caused by SWA. Line profiles indicate that fin shapes influence the modulation of the GRs as a function of Q_x. We demonstrate the characterization of complex $Si_{1-x}Ge_x$/ Si multilayers using RSMs and their line profiles which are relevant for lateral nanowire and nanosheet FETs. Above findings from RSM simulations clearly indicate the influence of variations in structural dimensions.

9:00am **EM+2D+AS+MI+MN+NS+TF-WeM-4 Nanoscale Depth and Lithiation Dependence of V_2O_5 Band Structure by Cathodoluminescence Spectroscopy***,*

Mitchell Walker*, N Pronin,* The Ohio State University*; A Jarry, J Ballard, G Rubloff,* University of Maryland, College Park*; L Brillson,* The Ohio State University

Vanadium pentoxide (V_2O_5) has attracted considerable interest for its potential use as a cathode for solid state lithium ion batteries. While researchers have studied the V_2O_5 lithiation charge/discharge cycle for over two decades, we are only now able to measure directly its electronic band structure from the surface to the thin film bulk and its changes with Li intercalation on a near-nanometer scale. We used depth-resolved cathodoluminescence spectroscopy (DRCLS) to monitor the changes in electronic structure from the free surface to the thin film bulk several hundred nm below. DRCLS measures optical transitions at 1.8-2, 3.1-3.2, 3.6-3.7, 4.0-4.1, and 4.6-4.7 eV between multiple conduction bands to the pristine (α) V_2O_5 valence band maximum in excellent agreement with $V_{3d}t_{2g}$ conduction band densities of states (DOS) predicted by density functional theory (DFT).[1] Triplet conduction band states at 1.8, 1.9, and 2 eV correspond to predicted V $3d_{xy}$–O_c $2p_x/2p_y$ hybridized states resulting from strong deviations of the unit cell VO_6 octahedra from cubic coordination correspond to optical absorption edges along the 3 crystallographic axes. With excitation depth increasing from < 10 to 125 nm calibrated by Monte Carlo simulations, the relative amplitudes and energies of these states change, signifying gradual changes in octahedral distortion. The band structure changes significantly with Li intercalation into $Li_xV_2O_5$ for x = 0, 1, and 2. Lithiation gradually removes the hybridized band and introduces a 2.4-2.7 eV V_{3d} t_{2g} band extending 50 nm (x=1) or 25 nm (x=2) into the surface. Higher (4.0 and 4.4 eV) features possibly related to a secondary phase dominate the spectra deep inside all V_2O_5 films near the battery electrode. Delithiation reintroduces the 1.8-2 eV split-off band although significantly narrowed by octahedral distortions. Overall, DRCLS shows that the lithiation cycle alters the V_2O_5 band structure on a scale of 10-100's of nm with lithiation. The direct measure of V_2O_5's electronic band structure as a function of lithiation level provided by DRCLS can help guide future battery engineering work as more efficient lithium ion batteries are developed. In particular, these unique electrode measurements may reveal in what ways lithiation changes V-$_2$O$_5$ irreversibly, as well as reveal methods to extend solid state battery life. MW and LJB acknowledge support from NSF grant DMR-18-00130. AJ and GR acknowledge Nanostructures for Electrical Energy Storage (NEES), a Department of Energy Office of Science Frontier Research Center.

1. V. Eyert and K.-H. Höck, "Electronic structure of V_2O_5: Role of octahedral deformation," Phys. Rev. B 57, 12727 (1998).

9:20am **EM+2D+AS+MI+MN+NS+TF-WeM-5 Electron Microscopy of Quantum Materials: From Learning Physics to Atomic Manipulation***,*

Sergei Kalinin*,* Oak Ridge National Laboratory **INVITED**

Atomically-resolved imaging of materials has become the mainstay of modern materials science, as enabled by advent of aberration corrected scanning transmission electron microscopy (STEM). In this talk, I will present the new opportunities enabled by physics-informed big data and machine learning technologies to extract physical information from static and dynamic STEM images. The deep learning models trained on theoretically simulated images or labeled library data demonstrate extremely high efficiency in extracting atomic coordinates and trajectories, converting massive volumes of statistical and dynamic data into structural descriptors. I further present a method to take advantage of atomic-scale observations of chemical and structural fluctuations and use them to build a generative model (including near-neghbour interactions) that can be used to predict the phase diagram of the system in a finite temperature and composition space. Similar approach is applied to probe the kinetics of solid-state reactions on a single defect level and defect formation in solids via atomic-scale observations. Finally, synergy of deep learning image analytics and real-time feedback further allows harnessing beam-induced atomic and bond dynamics to enable direct atom-by-atom fabrication. Examples of direct atomic motion over mesoscopic distances, engineered doping at selected lattice site, and assembly of multiatomic structures will be demonstrated. These advances position STEM towards transition from purely imaging tool for atomic-scale laboratory of electronic, phonon, and quantum phenomena in atomically-engineered structures.

11:00am **EM+2D+AS+MI+MN+NS+TF-WeM-10 Hot Electron Emission from Waveguide Integrated Graphene***,*

Ragib Ahsan*, F Rezaeifar, H Chae, R Kapadia,* University of Southern California

From free electron laser sources to electronic structure measurements, electron emission devices play an important role in a wide range of areas. Photoemission is one of the basic processes exploited in modern electron emission devices. However, higher-order processes like multiphoton absorption or optical field induced emission are necessary for efficient photoemission from high workfunction metallic emitters. Our work demonstrates a graphene emitter integrated on a waveguide that can evanescently couple with the photons delivered from a CW laser (405 nm) and registers photoemission at a peak power that is orders of magnitude lower than previously published results based on multiphoton and optical field induced emission processes. Coupling FDTD analysis of the waveguide to a rigorous quantum mechanical study of the scattering mechanisms and the tunneling processes in graphene, we have been able to model the emission current from the graphene emitter with good agreement to the experimental data. Our investigation reveals that the photoexcited electrons can go through three mutually competitive processes: (i) electron-electron scattering (ii) electron-phonon scattering and (iii) directly emission into the vacuum. Absorption of a photon causes a reduction in the tunnel barrier seen by the electron and the emission rate increases exponentially. Integration of graphene to the waveguide enables evanescent coupling between electrons and the photons causing almost 100% absorption of the photons. Our integrated photonics approach demonstrates an emission efficiency that is three orders of magnitude greater than free space excitation. These results suggest that integrating photonic elements with low dimensional materials such as 2D materials, nanoparticles, quantum dots, etc. can provide a new domain of efficient electron emission devices and integrated photonics.

11:20am **EM+2D+AS+MI+MN+NS+TF-WeM-11 Imaging Candidate Nanoelectronic Materials with Photoemission Electron Microscopy (PEEM)***,*

Sujitra Pookpanratana*, S Robey,* National Institute of Standards and Technology (NIST)*; T Ohta,* Sandia National Laboratories

The drive to produce smaller and lower power electronic components for computing is pushing the semiconductor industry to consider novel nanoscale device structures, not based solely on crystalline silicon. Continued innovation and progress towards novel nanoelectronic materials and devices in turn requires metrologies sensitive to electronic properties at these length scales. Tip-based imaging techniques provide electronic contrast with sub-nanometer resolution, however it is a local, scanning-based technique. Photoemission (or photoelectron spectroscopy) is the dominant technique to provide detailed electronic band structure information- level energies, dispersion, polarization dependence, etc. – but typically requires materials with millimeter, or larger, length scales. Photoemission electron microscopy (PEEM) can be employed to allow access to this vital information, providing full-field imaging capabilities sensitive to a variety of electronic contrast mechanisms at 10's of nanometers length scales. Here, we will present our results on imaging the impact of molecular dopants on multilayer tungsten disulfide (WS_2) employing the PEEM at the Center for Integrated Nanotechnologies within Sandia National Laboratories. We will also discuss the commissioning of a recently installed PEEM to perform complementary measurements at NIST-Gaithersburg.

Technological commercialization of transition metal dichalcogenides (TMDs) in nanoelectronics devices requires control of their electronic properties, such as charge carrier type and density, for specific device functionality. Conventional techniques for doping are problematic for atomically thin 2D materials. The sensitivity of mono- to few-layer (TMDs) to their local environment and interfaces can be employed *via* surface doping of molecules on TMDs to provide a promising route toward controllable doping. Investigations of surface doping for one to few layer WS_2 were performed using mechanically exfoliated WS_2 on a SiO_2/Si substrate that was then exposed to tris(4-bromophenyl)ammoniumyl hexachloroantimonate, a p-dopant molecule. PEEM was performed before and after p-dopant exposure. After doping, we find that the contrast of the surface WS_2 physical features change and valence band edge shifts about 0.8 eV away from the Fermi energy, consistent with p-doping. We will discuss the effects of molecular doping in terms of homogeneity and surface features across multiple WS_2 flakes. Lastly, we will discuss commissioning of a new PEEM instrument installed at NIST in 2019, using results of graphene to demonstrate imaging capability and energy resolution of this instrument.

11:40am **EM+2D+AS+MI+MN+NS+TF-WeM-12 Comparison of Features for Au and Ir Adsorbed on the Ge (110) Surface***, **Shirley Chiang**,* University of California, Davis*; R Xie, H Xing,* Donghua University, China*; T Rahman,* University of Central Florida*; C Fong,* University of California, Davis

Two ad-atoms of Au and Ir adsorbed, respectively, on the Ge(110) surface are studied by a first-principles algorithm based on density functional theory. The surface is modeled by a slab consisting of 108 Ge atoms with a 10 Å vacuum region. Hydrogen atoms are used to saturate the dangling orbitals at the other side of the vacuum region. Two cases of Au adsorption and one case of Ir are reported. The case of Ir has a large binding energy because of its small atomic size compared with the Ge atom, and the partially filled d-states. The total energy for each case is given, as are the energies for removing one ad-atom at a time and also both ad-atoms. The binding energy of each case is obtained by simply taking the energy difference between these configurations; this method is more realistic because the experimental data measured by LEEM and STM indicate that the collective motions of the ad-atoms do not allow the surface to relax to its equilibrium state.[1] For a large separation in the case of two Au atoms, there is a smaller binding energy than for one ad-atom. This can relate to the fact that the collective motions seen experimentally do not happen at a full monolayer coverage of ad-atoms.[1] Additional comparisons will be made to an atomic model for Ir/Ge(111) from STM measurements.[2]

[1] B. H. Stenger et al., Ultramicroscopy, 183, 72 (2017).

[2] M. van Zijll et al., Surf. Sci. 666, 90, (2017).

Support from NSF DMR-1710748 (SC, CYF); NSF DMR-1710306 (TSR); National Natural Science Foundation of China Grants 61376102, 11174048 and computational support from Shanghai Supercomputer Center (RKX, HZX).

12:00pm **EM+2D+AS+MI+MN+NS+TF-WeM-13 Reference Materials for Localization Microscopy***, C Copeland, R Dixson, L Elliott, B Ilic,* National Institute for Science and Technology (NIST)*; D Kozak, K Liao,* FDA, National Institute for Science and Technology (NIST)*; J Liddle,* NIST Center for Nanoscale Science and Technology*; A Madison,* National Institute for Science and Technology (NIST)*; J Myung,* FDA*; A Pintar, **Samuel Stavis**,* National Institute for Science and Technology (NIST)

As the diffraction limit fades away into the history of optical microscopy, new challenges are emerging in super-resolution measurements of diverse systems ranging from catalysts to therapeutics. In particular, due to common limitations of reference materials and microscope calibrations, many localization measurements are precise but not accurate. This can result in gross overconfidence in measurement results with statistical uncertainties that are apparently impressive but potentially meaningless, due to the unknown presence of systematic errors that are orders of magnitude larger. To solve this fundamental problem in measurement science, we are optimizing and applying nanofabrication processes to develop reference materials for localization microscopy, and demonstrating their use in quantitative methods of microscope calibration.

Our program consists of two complementary approaches. In the first, involving applied metrology, we are developing reference materials such as aperture arrays that can serve as standalone artifacts for widespread deployment. This approach will require the application of critical-dimension metrology to establish the traceability of master artifacts, and their use to calibrate a super-resolution microscope for high-throughput characterization of economical batches of reference materials. In the second approach, involving fundamental research, we are demonstrating the application of reference materials and calibration methods in our own experimental measurements. Most interestingly, achieving vertical integration of our two approaches and the unique capabilities that result, we are building reference materials into measurement devices for in situ calibration of localization measurements for nanoparticle characterization.

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Complex Oxides: Fundamental Properties and Applications Focus Topic

Room A220-221 - Session OX+EM+MI+SS-WeM

Electronic and Magnetic Properties of Complex Oxide Surfaces and Interfaces

Moderators: Yingge Du, Pacific Northwest National Laboratory, Vincent Smentkowski, GE Global Research Center

8:00am **OX+EM+MI+SS-WeM-1 Charge Transfer in Lanthanum Ferrite-Strontium Nickelate Superlattices***, **Le Wang**, Z Yang, M Bowden,* Pacific Northwest National Laboratory*; J Freeland,* Argonne National Laboratory*; Y Du, S Chambers,* Pacific Northwest National Laboratory

Charge transfer at oxide interfaces can drive emergent phenomena that do not occur in the bulk, thereby significantly enriching our fundamental understanding of these material systems and their applications. Designing oxide heterostructures and seeking new and novel interfacial phenomena has been an active area of research for some time. We have synthesized a series of $[(LaFeO_3)_m/(SrNiO_{3-d})_n]_z$ ($[(LFO)_m/(SNO)_n]_z$) superlattices (SLs) (z = 7 to 21) by oxide molecular beam epitaxy on $(LaAlO_3)_{0.3}(Sr_2AlTaO_6)_{0.7}$ (LSAT) (001) substrates. *In situ* RHEED patterns and x-ray diffraction measurements reveal a high degree of structural quality in the SLs. X-ray photoemission spectroscopy (XPS) shows that the Fe is Fe^{4+} in the $(LFO_1/SNO_1)_{21}$ SL. However, the Fe 2p binding energy shifts to lower values with increasing LFO layer thickness in $(LFO_m/SNO_1)_z$ SLs, suggesting that the volume averaged Fe valence decreases. Fe L-edge X-ray absorption spectroscopy (XAS) measurements corroborate the XPS results, indicating that Fe is 4+ for the $(LFO_1/SNO_1)_{21}$ SL and mostly 3+ for the $(LFO_5/SNO_1)_{10}$ SL. On the other hand, Ni L-edge XAS shows that Ni valence is Ni^{3+} for the $(LFO_1/SNO_1)_{21}$ SL as is also true for insulating $NdNiO_3$, suggesting that the Ni layers in this SL are insulating, which is consistent with our in-plane transport measurements. However, for the $(LFO_5/SNO_1)_{10}$ SL, the Ni valence is larger than 3+. The measured energy shifts suggest that Ni is close to 4+. The thicker LFO layer in the $(LFO_5/SNO_1)_{10}$ SL may result in a larger band offset and create a potential well to trap the holes in the Ni layer, inducing the formation of Ni^{4+}. Our ongoing studies are probing the impact of the SNO layer thickness on material structure as well as the evolution of the Fe and Ni valences in $(LFO_5/SNO_n)_z$ SLs. Additional planned experimental and theoretical investigations will address how charge transfer from Fe to Ni occurs at the LFO/SNO interface, and how to stabilize the unusual high 4+ valence in Fe^{4+} and Ni^{4+} by means of interfacial engineering.

8:20am **OX+EM+MI+SS-WeM-2 Self-healing Growth of LaNiO$_3$ on Mixed-terminated (LaAlO$_3$)$_{0.3}$-(Sr$_2$AlTaO$_6$)$_{0.7}$**, ***Friederike Wrobel****, H Hong, S Cook, T Andersen, D Hong, C Liu, A Bhattacharya, D Fong,* Argonne National Laboratory

Epitaxial LaNiO$_3$ (LNO) thin films and superlattices are known to be antiferromagnetic and weakly insulating for LNO thicknesses of 2 unit cells but paramagnetic and metallic for higher LNO thicknesses [1]. The quality of the single-crystal substrate surface, and in particular the chemical composition of the surface, is known to be a key factor governing the quality of the deposited thin film. For SrTiO$_3$ (001) substrates, there are well-established preparation methods to ensure that the surface is TiO$_2$-terminated and atomically smooth; the only features that appear with atomic force microscopy are the regular steps and terraces associated with crystal miscut. SrTiO$_3$ is therefore often preferred as a substrate over other materials like (LaAlO$_3$)$_{0.3}$-(Sr$_2$AlTaO$_6$)$_{0.7}$ (LSAT), whose surface composition is harder to control. Interestingly, for unknown reasons, the highest quality LaNiO3 thin films have been grown on mixed-terminated, untreated LSAT (001) substrates [2, 3]. At present, very few detailed studies have been conducted regarding the precise influence of the substrate on thin film growth behavior due to the need for an in-situ, atomic-scale characterization technique. Exploiting an in-situ, oxide molecular beam epitaxy (MBE) chamber at the Advanced Photon Source, we were able to monitor the deposition of thin films of LNO on LSAT (001) substrates with different surface compositions. Both non-resonant and resonant (Sr K-edge) X-ray scattering measurements were conducted at several points during the growth process. We observed the formation of atomically smooth, high-quality LNO films regardless of the initial substrate surface composition, suggesting that any excess, non-stoichiometric material on the initial LSAT substrate rises to the surface during deposition. With atomic layer-by-atomic layer MBE under the right conditions, we can therefore achieve self-healing growth behavior of complex oxides on top of mixed-terminated substrates. We will discuss details of the in-situ growth measurements and the methods used to determine the atomic and chemical structures.

1. Frano, A., et al., *Orbital Control of Noncollinear Magnetic Order in Nickel Oxide Heterostructures.* Physical Review Letters, 2013. **111**(10): p. 106804.

2. Liu, C., et al., *Counter-thermal flow of holes in high-mobility LaNiO3 thin films.* Physical Review B, 2019. **99**(4): p. 041114.

3. Wrobel, F., et al., *Comparative study of LaNiO3/LaAlO3 heterostructures grown by pulsed laser deposition and oxide molecular beam epitaxy.* Applied Physics Letters, 2017. **110**(4): p. 041606.

8:40am **OX+EM+MI+SS-WeM-3 Optoelectronics with Oxides and Oxide Heterostructures**, ***Alexander Demkov,*** University of Texas at Austin **INVITED**

Si photonics is a hybrid technology combining semiconductor logic with fast broadband optical communications and optical information technologies. With the increasing bandwidth requirement in computing and signal processing, the inherent limitations in metallic interconnection are seriously threatening the future of traditional IC industry. Silicon photonics can provide a low-cost approach to overcome the bottleneck of the high data rate transmission by replacing the original electronic integrated circuits with photonic integrated circuits. The development has proceeded along several avenues including mounting optical devices based on III-V semiconductors and/or LiNbO$_3$ (LNO) on Si chips, incorporation of active optical impurities into Si, and utilization of stimulated Raman scattering in Si. All these approaches have had limited success. Recently, another path to Si photonics through epitaxial integration of transition metal oxide films was demonstrated when an effective electro-optic (Pockels) coefficient of BaTiO$_3$ (BTO) films epitaxially grown on Si *via* an SrTiO$_3$ buffer was reported to be an order of magnitude larger than that in commercially-available LNO modulators. More generally, epitaxial growth of SrTiO$_3$ on Si(001) enables monolithic integration of many functional perovskite oxides on Si, including ferroelectric BTO, ferromagnetic LaCoO$_3$, photocatalytic TiO$_2$ and CoO, and many others.

In this talk, I will focus on two materials systems integrated on Si (001) and well-suited for implementation in the next-generation optical technologies: SrTiO$_3$/LaAlO$_3$ quantum wells and Pockels-active BTO thin film heterostructures. Both materials systems are promising for use in a wide variety of optical and electro-optical devices central to integrated photonic technologies, including quantum cascade lasers, photodetectors, electro-optic modulators and switches. The resulting devices achieve refractive index tuning with power consumption many orders of magnitude less than previously reported. Taken together, these two approached will hopefully open the door for the development of new kinds of optical and electro-optical devices for use in integrated photonics technologies.

9:20am **OX+EM+MI+SS-WeM-5 Medard W. Welch Award Lecture: Defect-Mediated Coupling of Built-in Potentials at Buried Interfaces Involving Epitaxial Complex Oxides**, ***Scott. A Chambers***[1], Pacific Northwest National Laboratory **INVITED**

Semiconductor-based devices are of broad importance, not only in electronics, but also in energy technology. Internal electric fields dictate the flow of charge that occurs both laterally and vertically. The associated potential profiles can be approximated from electronic transport data, and also calculated via Poisson-Schrodinger modeling, provided the properties of the constituent materials and interface structures are sufficiently well understood. These approaches work well for heterostructures involving, for instance, III-V semiconductors. However, when complex oxides are involved, they become unreliable because of poorly understood defects that can be present. There is, therefore, a critical need for new methods to enable the determination of band-edge profiles in heterostructures involving these materials.

The SrTiO$_3$/Si(001) interface has been a prototypical system for understanding the materials physics and electronic structure of crystalline oxides on semiconductors. Thinner films (a few unit cells, u.c.) are known to result in flat-band heterojunctions in which the valence (conduction) band offset is large (small). However, we have recently found that thicker films (~30 u.c.) of SrNb$_x$Ti$_{1-x}$O$_3$ ($0 \le x \le 0.2$) on intrinsic Si(001) result in completely different electronic structures. Transport data suggest sharp upward band bending in the Si, leading to hole gas formation at the interface, and a large (~2 eV) built-in potential in the SNTO, along with surface depletion. We have probed these buried interfaces using hard x-ray photoelectron spectroscopy (HAXPES). The resulting core-level spectra exhibit unusual features not seen in thinner films, and not credibly ascribed to secondary phases or many-body effects. In order to interpret these line shapes, we hypothesize that they result from large built-in potentials within the system. We have developed an algorithm to extract these potential profiles by fitting heterojunction spectra to linear combinations of spectra from phase-pure, flat-band materials, summed over layers within the probe depth, each with a binding energy characteristic of the potential at each depth. This approach leads to excellent agreement with experiment and band-edge profiles completely consistent with those from transport data. Moreover, we find that the built-in potentials extracted from HAXPES on the Si side of the interface are in quantitative agreement with those resulting from solving Poisson's equation using the SIMS profile for in-diffused oxygen from the STO. Oxygen is a shallow donor in Si, and assuming 100% donor ionization, along with the ^{18}O SIMS depth profile, leads to near-perfect agreement with HAXPES.

11:00am **OX+EM+MI+SS-WeM-10 Spin Transport Studies on Epitaxial Ultrathin SrIrO$_3$ Films Grown using Pulsed Laser Deposition (PLD)**, ***M S Ramachandra Rao,*** Indian Institute of Technology, India*; K Sethupathi, T Suraj, S Suresh,* Indian Institute of Technology Madras, India

Generation, transportation and detection of spin in a controlled manner are very important in spintronic devices for efficient switching mechanisms in a magnetic tunnel junction (MTJ)[1,2,3]. The conversion of charge current to spin current is known as spin Hall effect (SHE) and the inverse phenomenon is inverse SHE (ISHE). The detection of spin is usually realized by the ISHE. Spin Hall magnetoresistance (SMR) arises due to the combined effect of SHE and ISHE in a bilayer heterostructures consisting of a ferromagnetic (or ferrimagnetic) insulator (FMI) and a normal metal (NM). Magnetic Proximity Effect (MPE) observed in YIG/Pt complicates the spin transport scenario with additional effects such as Anomalous Hall effect (AHE) which attenuates the SMR signal.[4,5]. Our group has successfully studied Ga: ZnO insertion on Bi: YIG/Pt and observed SMR signals[6]. Correlated metal oxide SrIrO$_3$ is a potential candidate which can replace Pt because of its high spin-orbit coupling.

We have deposited SrIrO$_3$ thin films with thickness from 3 nm to 10 nm using pulsed laser deposition on LSAT(001) substrate with LaMnO$_3$ as a buffer layer. Detailed structural measurements have been carried out to understand the strain induced in the bilayer system by varying oxygen partial pressure during deposition of LaMnO$_3$. Also, spin transport studies have been carried out since LaMnO$_3$ is an A-type antiferromagnet. Angle-dependent magnetic measurements performed on these bilayer samples

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[1] **Medard W. Welch Award Winner**

shows SMR, as well as anisotropic magnetoresistance (AMR) and the AMR part, is dominating over SMR. A particular thickness of $SrIrO_3$ shows a crossover from negative magnetoresistance to positive magnetoresistance. I will be presenting our experimental observations on spin transport studies carried out in these bilayers.

References

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11:20am **OX+EM+MI+SS-WeM-11 Structural and Dielectric Characterization of Epitaxial Entropy-Stabilized Oxide Thin Films*, George Kotsonis*,** *J Maria,* Pennsylvania State University

The emergence of entropy-stabilized oxides (ESOs) represents a new paradigm for complex oxide engineering. The large configurational entropy of ESOs facilitates mixing of chemically dissimilar cations in significant proportions. ESO research continues to intensify as the oxide community works toward a thorough understanding of structure-property-synthesis relationships. Due to inherent metastability, high energy, non-equilibrium synthesis techniques are well suited for ESO fabrication. In particular, laser ablation has excelled at producing high quality epitaxial ESO thin films, which provide a platform for fundamental characterization.

We present the growth and characterization of $Ba(Ti_{0.2}Sn_{0.2}Zr_{0.2}Hf_{0.2}Nb_{0.2})O_3$ and similar Barium-based perovskite structured ESO thin films grown by laser ablation. Crystal structure, surface morphology, and optical properties are characterized by X-ray diffraction, atomic force microscopy, and ellipsometry respectively. Epitaxial thin film capacitor structures were fabricated to characterize the frequency, voltage, and temperature dependence of electrical properties.

By exploiting the entropy-stabilized nature of ESOs, we demonstrate the incorporation of significant amounts of aliovalent cation pairs (*e.g.* $Sc^{3+}Ta^{5+}$) in hopes of producing nano-polar regions supporting a dispersive dielectric response similar to relaxor ferroelectrics. Additionally, we explore compositional space in search of a phase boundary between a high-symmetry ESO phase and a lower symmetry end-member. Compositions at such a boundary may exhibit phase instability and enhanced dielectric functionality similar to compositions at or near a morphotropic phase boundary. The compositional degrees of freedom available in ESO systems provide new avenues for property tuning and studying the effects of extreme chemical disorder on dielectric properties.

11:40am **OX+EM+MI+SS-WeM-12 Oxygen Vacancy-Mediated Epitaxy: $TiO_2(111)/Al_2O_3(0001)$ and Ferromagnetic $Cr_2O_3(0001)/TiO_2(111)$**, *C Ladewig, F Anwar, **Jeffry Kelber,*** University of North Texas*; S Shah, P Dowben,* University of Nebraska-Lincoln

The formation of all-oxide heterostructures comprising multiferroic oxides interfaced with appropriate semiconducting substrates is a promising path towards low power, voltage-switchable spintronics, including non-volatile memory and multi-functional logic devices. At the same time, the necessary scaling of film thicknesses to the nm range can induce structures and properties sharply different than those of the bulk. We report here in situ XPS, LEED, EELS and ex-situ MOKE data on the growth and properties of $Cr_2O_3(0001)$ on $TiO_{1.7}(111)$ on $Al_2O_3(0001)$. The data indicate that the presence of O vacancies during film growth can mediate the further growth of oxides with unusual structures and properties. These data show that (a) O vacancies during initial stages of film growth yield a TiO_2 film of an unusual crystallographic orientation and structure; and that (b) this leads to growth of an epitaxial Cr_2O_3 layer exhibiting magnetic ordering above the expected Néel temperature of thin film chromia - indicative of a strained chromia lattice due to epitaxial growth on a substrate with a lattice constant of 5.1 Å, compared to the bulk chromia lattice constant of 4.9 Å. Molecular beam epitaxy (MBE) of Ti at 500 K in 10^{-6} Torr O_2 on $Al_2O_3(0001)$ initially yields $TiO_{1.7}(111)$ with the structure of corundum phase Ti_2O_3 (a = b=5.1 Å). Further deposition and annealing in O_2 results in stoichiometric $TiO_2(111)$, but with the same lattice structure and orientation as $Ti_2O_3(111)$, and with a total thickness of 5 nm. This is sharply different from the generally observed growth of $TiO_2(001)$ on $Al_2O_3(0001)$. MBE of ~ 1 monolayer of Cr on $TiO_2(111)$ yields hexagonally-ordered Cr_2O_3 and the formation of titania oxygen vacancies. MOKE measurements confirm that this chromia layer is magnetically ordered at 280 to 315 K, likely antiferromagnetically ordered, with exchange bias coupling to the $TiO_{1.7}(111)$ substrate. O vacancies in the $TiO_2(111)$ lattice exhibit weak ferromagnetic behavior, as is evident in the In-plane MOKE, enhancing the canting of the magnetism away from the thin film normal, which is expected for the $Cr_2O_3(0001)$ alone. These data demonstrate that careful control of initial growth conditions and film stoichiometry during oxide MBE can template the subsequent growth of stoichiometric oxide heterostructures with non-bulk like structures and properties.

Acknowledgement: Work at UNL was supported in part by the Semiconductor Research Corporation (SRC) as task 2760.002 and NSF through ECCS 1740136.

12:00pm **OX+EM+MI+SS-WeM-13 Incorporation of Ti into Epitaxial Films of Magnetite*, Tiffany Kaspar*,** *S Spurgeon, D Schreiber, S Taylor, M Bowden, S Chambers,* Pacific Northwest National Laboratory

Magnetite, Fe_3O_4, exhibits metallic conductivity via electron hopping between Fe^{2+} and Fe^{3+} occupying octahedral sites in the spinel lattice. As Ti^{4+} is doped into the octahedral sites of magnetite (the titanomagnetite series), an equal fraction of Fe^{3+} is reduced to Fe^{2+} to maintain charge neutrality. The site occupancies of Fe^{2+} and Fe^{3+} determine the transport properties of the titanomagnetite series; the end-member ulvöspinel, Fe_2TiO_4, exhibits *p*-type semiconducting transport properties. The Fe^{2+}/Fe^{3+} site occupancy remains controversial, but is likely in part a function of the lattice strain induced by doping smaller Ti^{4+} into the lattice. Here, we have deposited titanomagnetites and ulvöspinel as well-defined epitaxial thin films on MgO, $MgAl_2O_4$, and Al_2O_3 substrates by oxygen-plasma-assisted molecular beam epitaxy. The incorporation of Ti into the magnetite lattice is found to depend strongly on deposition conditions and substrate orientation. We have characterized the crystalline structure, phase segregation, and surface morphology with XRD, STEM/EDS, APT, and AFM, and related these to the kinetic and thermodynamic factors determined by the deposition conditions. The Fe valence state is evaluated with *in situ* XPS. The impact of film structure and Fe oxidation state on the electrical transport properties of the films will be discussed.

Plasma Science and Technology Division
Room B131 - Session PS+EM-WeM
Plasma Processing of Materials for Energy

Moderators: Ankur Agarwal, KLA-Tencor, Saravanapriyan Sriraman, Lam Research Corp

8:00am **PS+EM-WeM-1 Plasma Processes for High Efficiency Multi-Junction Solar Cells Fabrication*, Maxime Darnon*,** *M Volatier, P Albert, M de Lafontaine, P St-Pierre, G Hamon,* LN2, CNRS / Université de Sherbrooke, 3IT, Canada*; C Petit-Etienne, G Gay, E Pargon,* LTM, CNRS / Université Grenoble Alpes, France*; V Aimez, S Fafard, A Jaouad,* LN2, CNRS / Université de Sherbrooke, 3IT, Canada **INVITED**

Multijunction solar cells provide the highest efficiency for solar energy conversion into electricity. With record efficiency above 45%, they are used in concentrated photovoltaic systems where their cost is mitigated by the sunlight concentration. Conventional technics for such solar cells' fabrication include III-V materials epitaxy on germanium, electrodes lift off, antireflective coating deposition by physical vapor deposition and isolation by saw dicing. In this presentation, we will show how plasma processes can advantageously be used to replace some of these steps and how it could enable the fabrication of new architectures of solar cells.

A low-damage III-V plasma etching step can isolate the solar cells one to the other before the mechanical saw dicing. This reduces the density of recombination centers at the edge of the solar cells and provides therefore a higher open circuit voltage. Deep germanium plasma etching can also be used for solar cells dicing with trenches as small as 10 µm. As an alternative to physical vapor deposition, plasma enhanced chemical vapor deposition can coat high transparency silicon nitride and silicon oxide that form an excellent anti-reflective coating and passivate surface recombination centers.

In addition to their benefit for conventional solar cells fabrication, these plasma-based processes also provide opportunity for the fabrication of new kinds of multijunction solar cells, such as ultra small solar cells (<0.07 mm^2), front-side contacted solar cells, back-side contacted solar cells, and through cell via contacted solar cells.

8:40am **PS+EM-WeM-3 Combinatorial Synthesis of Ternary Oxides by Reactive Sputtering for CdTe Solar Cells***, **Yegor Samoilenko**, G Yeung, C Wolden,* Colorado School of Mines

Polycrystalline CdTe-based solar cells have reached efficiencies of over 22% in the recent years. The road towards high V_{oc} and 25% devices requires a combination of low interface recombination velocity, higher lifetime, and higher carrier concentration in the CdTe absorber. It was recently demonstrated that the impact of the interface recombination on the performance of the device is more pronounced as carrier concentration and lifetime increase. Magnesium zinc oxide (MZO) has been identified as a transparent emitter that enables high efficiency in CdTe based solar cells. By controlling the alloy composition one may tune the conduction band alignment with CdTe absorber at the front interface to reduce recombination. Most previous work has employed MZO targets sputtered in Ar. However there are open questions as to what the optimal composition, its stability, and sensitivity to subsequent processing.In this work we perform a combinatorial study of MZO buffer layer prepared by co-sputtering of Zn and Mg in oxygen-containing atmosphere. Combinatorial libraries are formed with a band gap variation of more than 0.4 eV across a 2 inch substrate. These are integrated into standard CdTe to determine the optimal composition based on using J-V characteristics. In addition, the stability of these films is assessed by surface spectroscopy, and routes to stabilize performance are introduced.

9:00am **PS+EM-WeM-4 Potential Applications of TiN-based Plasmonic Nanoparticles: From Plasmon-induced Chemistry to Photothermal Absorption***, A Alvarez Barragan, C Berrospe Rodriguez, **Lorenzo Mangolini**,* University of California, Riverside

The light-harvesting capacity of plasmonic nanoparticles has recently garnered attention in the synthesis of plasmon-driven photocatalysts. Gold and silver have been used to successfully drive hydrogen dissociation and CO oxidation reactions by injecting hot electrons into molecules adsorbed to their surface. However, the chemical instability of silver and the low thermal stability of both metals, in addition to their high cost, 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 visible-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 synthesis of TiN nanoparticles via a non-thermal plasma method. It also highlights the potential of this material as an alternative in plasmonic catalysis and as a high-temperature-resistant photothermal absorber. 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. Platinum nanoparticles were subsequently deposited on the TiN by photo-induced reduction of an aqueous solution of chlorplatinic acid (H_2PtCl_6). The reduction of the precursor metal was driven by electron hole pair generation via plasmon decay. The addition of methanol as a hole scavenger increased the electron lifetime, leading to the obtention of metallic platinum. This reaction occurred at temperatures below 40°C under visible light illumination. In addition, a novel $TiN@SiO_xN_y$ core-shell structure is facilitated by the modular capabilities of the non-thermal plasma synthesis method. The plasmon peak of the extinction spectrum of the core-shell particles is enhanced by 60% compared to the uncoated TiN particles. The high temperature resistance of these heterostructures is also demonstrated, as their optical properties remain stable at 700 °C under vacuum and at 400 °C in air. This work strengthens the case for alternative plasmonic materials in fields dominated by precious metals, and heavily driven by materials cost.

9:20am **PS+EM-WeM-5 Plasma-induced Strain in MoS_2 Films for the Electrochemical Hydrogen Evolution Reaction***, T Liu, X Liu, **Souvik Bhattacharya**,* Case Western Reserve University*; Z Ye, R He,* Texas Tech University*; X Gao, R Akolkar, R Sankaran,* Case Western Reserve University

There has been recent interest in growing layered materials such as molybdenum disulfide (MoS_2) over large areas for electronic and energy applications. One such approach is chemical vapor deposition (CVD) in which vapor precursors are thermally decomposed to nucleate a thin film at the surface of a substrate. A plasma may also be employed to assist in decomposition of the precursor molecule through gas-phase excitation, for example in plasma-enhanced CVD (PECVD) or plasma-enhanced atomic layer deposition (PEALD). Here, we report a plasma-assisted approach which is fundamentally different than these deposition techniques which we term plasma-enhanced chemical film conversion (PECFC). Precursor films are first prepared as a thin film on a substrate from liquids and subsequently converted by a combination of heating and plasma treatment. The process is additive, in that the precursor is only present where it is desired and there is little materials wastage, and substrate-independent, by circumventing the need for adsorption, allowing direct growth on application-specific substrates.

In this talk, we will present results for the synthesis of MoS_2 films and their application as electrocatalysts for the hydrogen evolution reaction (HER). A single-molecule precursor, ammonium tetrathiomolybdate (ATM), was first dispersed in solution with linear polyethylenimine (L-PEI) and spin-coated to produce a well-defined thin film less than 50 nm thick. The precursor film was then treated by an atmospheric-pressure dielectric barrier discharge (DBD) in a background of argon and hydrogen gas (80:20) at 500 ^{o}C. Conversion to crystalline MoS_2 was confirmed by X-ray diffraction and micro Raman spectroscopy. Atomic force microscopy was performed to study possible nucleation and growth mechanisms by varying the growth temperature and treatment time. The chemical composition was analyzed by X-ray photoelectron spectroscopy which showed an ideal stoichiometric ratio of 1:2 Mo:S.

A potential application of MoS_2 films is HER because it is composed of earth abundant elements and has been shown to be highly active through its edge sites. We carried out a systematic study of the origin of HER activity in our films, both after initial conversion and after several other post-synthesis treatments . The investigation showed that our initially-converted films have tensile strain leading to intrinsic activity that is comparable to previously reported sulfur vacancy generation by post-synthesis plasma treatment steps. In our case, the strain is induced in the initial fabrication step, providing a simpler and more scalable process to produce efficient HER electrocatalysts.

9:40am **PS+EM-WeM-6 Comparison of Pulsed and Continuous Wave Argon Plasmas for the Synthesis of Vertical Graphene Nanosheets***, **Zoe Mann**, E Fisher,* Colorado State University

Vertical graphene nanosheets (VGNs) have unique structural and electronic properties that make them applicable in fields such as energy storage, electronics, and sensing. VGNs are often grown using high-power, high-temperature processes and hazardous or unsustainable precursors such as methane. For this reason, we sought to develop a simple, efficient, and more environmentally-friendly way to synthesize VGNs. In this work, VGNs are synthesized from butter or coconut oil (sustainable, non-toxic precursors) spread on a Ni foam or Cu substrate and then treated with a high peak power pulsed plasma process. The materials formed through this process are compared to those produced with a continuous wave treatment of equivalent power and a low peak power pulsed plasma treatment, as well as to the untreated material. We used a range of characterization techniques to assess the materials, including scanning election microscopy (SEM), X-ray photoelectron spectroscopy (XPS), Raman spectroscopy, and cyclic voltammetry, providing data on the morphology, surface chemistry, bulk characteristics, and electrochemical performance, respectively. SEM imaging shows that VGNs grown by the high power pulsed PECVD technique have high surface area and abundant ultra-thin edges. XPS analysis of untreated butter and the low-power pulsed plasma treated samples reveals binding environments consistent with the chemical composition of triglycerides (the primary chemical component in butter/oil), whereas the XPS and Raman spectra of VGNs indicate the presence of sp^2-hybridized carbon. Notably, cyclic voltammograms of VGNs formed on Ni foam are characteristic of a capacitor, and these materials do not exhibit the deleterious side reactions found with VGNs formed on the Cu substrate. To better understand the underlying chemistry occurring during plasma treatment, optical emission spectroscopy data were collected, revealing key information on species important for VGN synthesis, such as atomic and molecular carbon.

Materials and Processes for Quantum Information, Computing and Science Focus Topic
Room B231-232 - Session QS+2D+EM+MN+NS+VT-WeM

Material Systems and Applications for Quantum Sciences

Moderators: Mena Gadalla, Harvard University, Kai Xiao, Oak Ridge National Laboratory

8:00am **QS+2D+EM+MN+NS+VT-WeM-1 Quantum Information at the Molecular Foundry - An Overview of New Toolsets for QIS Research***, **Adam Schwartzberg**, S Cabrini, D Ogletree, A Weber-Bargioni,* Lawrence Berkeley National Laboratory (LBNL)

The fundamental unit of quantum computation and sensing is the qubit, and many physical systems have been investigated for practical realization. These include superconducting Josephson junction circuits, color centers, and isolated cold atoms or ions. Superconducting qubit circuits (SCQBs) being one of the most promising avenues to quantum computation. However, there are limitations to their practical application due to noise sources which shorten their functional lifetime.

In this talk I will introduce a suite of integrated, high-fidelity fabrication instrumentation that will allow new communities of users to investigate the fundamental limits of state-of-the-art quantum systems at the Molecular Foundry. We will enable users to understand existing systems and design new ones by creating a quantum fabrication toolset for directed growth of conventional and novel materials, advanced lithography and pattern transfer paired with in- and ex-situ surface characterization.

Three key QIS fabrication capabilities at the Molecular Foundry:

A robotic fabrication cluster system with materials deposition, including atomic layer and physical vapor depositions, plasma etching, and analytical characterization instrumentation, all automated by and contained within a vacuum sample handling robot.

A high resolution electron beam writing system will allow quantum device patterning with complete flexibility in feature shape, density and size, enabling nanoscale feature control.

A low temperature transport measurement system will allow for the investigation of novel materials for superconductors and dielectrics and “close the loop” between design and fabrication, proxy measurements such as interface characterization, and actual performance of quantum computation and sensing elements.

This instrumentation suite will enable the elucidation of chemical composition, structure, location, and size of microscopic noise sources in a superconducting quantum system, understanding the fabrication steps that introduced such noise sources, and developing fabrication approaches that minimize their presence.

I will also discuss ongoing and new research directions at the Molecular Foundry through internal staff and external user research.

8:20am **QS+2D+EM+MN+NS+VT-WeM-2 Quantum Vacuum Metrology to Advance Quantum Science Capabilities***, **Jay Hendricks**, J Ricker, K Douglass,* National Institute of Standards and Technology (NIST)*; J Fedchak, J Scherschligt,* National Institute of Sandards and Technology (NIST)

NIST is developing a series of next generation pressure and vacuum standards that will serve as a basis for key vacuum technology platforms required for emerging quantum science applications. The production of quantum sensors and devices is anticipated to require extremely demanding process control with exact knowledge of background residual gas, process chamber pressure, and accurate measurement of gas pressure feedstocks.

In 2019, National Metrology Institutes around the world worked to redefine the international system of units, the SI, such that the base units are now based on fundamental constants.

Moving forward, the next generation of pressure and standards will provide a new route of SI traceability for the pascal. By taking advantage of both the properties of light interacting with a gas and that the pressure dependent refractive index of helium can be precisely predicted from fundamental, first-principles quantum-chemistry calculations, a new route of realizing the pascal has been demonstrated. This talk will briefly cover the classical methods of realizing pressure that have served the metrology community well for the past 375 years. And then will take a deeper dive into the next generation of light-based pressure standards that will enable the elimination of mercury manometers, replacing them with a smaller, lighter, faster, and higher precision standards. From a metrology stand point, the new quantum-based SI pascal will move us from the classical force/area definition, to an energy density (joules per unit volume) definition. Should the technique be further miniaturized, it will lead to a revolution in pressure metrology, enabling a photonics-based device that serves both a gas pressure sensor and a portable gas pressure standard all in one.

NOTE: this topic is appropriate for VT sessions as well but thought it would be interesting to the broader audience that is interested in emerging quantum-based technologies that are needed to advance the field of quantum science.

8:40am **QS+2D+EM+MN+NS+VT-WeM-3 Quantum Control of Spins in Silicon Carbide with Photons and Phonons***, **David Awschalom**, S Whiteley, G Wolfowicz, K Miao,* University of Chicago **INVITED**

There are numerous efforts to embrace solid-state defects and construct quantum systems to enable new information technologies based on the quantum nature of the electron. Current studies include semiconductors with incorporated point defects, whose quantum mechanical spin properties allow a fundamentally different means to process information. In particular, interfacing solid-state defect electron spins to other quantum systems is an ongoing challenge. Here we demonstrate electrically driven coherent quantum interference in the optical transition of single divacancies, enabling new control of the spin-photon interface [1]. By applying microwave frequency electric fields, we coherently drive the excited-state orbitals and induce Landau-Zener-Stückelberg interference fringes in the resonant optical absorption spectrum. Furthermore, we develop a stroboscopic X-ray diffraction imaging technique that provides direct imaging and quantitative measurement of local strain at the nanometer scale. In conjunction with the fabrication of surface acoustic wave resonators, we mechanically drive coherent Rabi oscillations between arbitrary ground-state spin levels, including magnetically forbidden spin transitions, allowing for acoustic quantum control of local spins in silicon carbide and the exploration of spin-phonon coupling in the solid state [2]. These properties establish divacancies as strong candidates for quantum communication and hybrid system applications, where simultaneous control over optical and spin degrees of freedom is paramount.

[1] K. C. Miao *et al*., arxiv: 1905.12780

[2] S. J. Whiteley *et al*., Nature Phys. **15**, 490 (2019)

9:20am **QS+2D+EM+MN+NS+VT-WeM-5 Tunable Control over InSb(110) Surface Conductance Utilizing Charged Defects***, **Robert Walko**, S Mueller, S Gant, J Repicky, S Tjung, E Lang, E Fuller, K Werner,* The Ohio State University*; F Bergmann,* Bergmann Messgeraete Entwicklung*; E Chowdhury, J Gupta,* The Ohio State University

In this work we present a scanning tunneling microscopy (STM) study of tip-induced switching of charge states in individual indium adatoms on the InSb(110) surface. These adatoms are deposited onto the surface by controlled voltage pulses between the STM tip and the surface. We observe them in two distinct charge states: positive and neutral. Adatom-induced band bending from the positively charged state has been observed to induce a tenfold increase in surface conductance relative to the charge neutral state, the effect of which can be observed >100nm away from the indium adatom. When the STM tip is brought sufficiently close to the defect, electrons can tunnel from the tip to the defect and cause the charge state to switch from positive to neutral. During imaging, this switching leads to a “crater” feature around the defect due to the lower conductance of the charge neutral state. The spatial extent of the crater can be tuned via the applied bias voltage, the tunneling set-point current, and photoillumination of the surface. We explain this phenomenon using a model of competing rates between the filling and emptying of the defect state, similar to dangling bonds on the Si(111) surface.

This work acknowledges funding from the DOE (# DE-SC0016379)

9:40am **QS+2D+EM+MN+NS+VT-WeM-6 Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform***, **Matthew R. Rosenberger,*** U.S. Naval Research Laboratory*; C Dass,* Air Force Research Laboratory*; H Chuang, S Sivaram, K McCreary,* U.S. Naval Research Laboratory*; J Hendrickson,* Air Force Research Laboratory*; B Jonker,* U.S. Naval Research Laboratory

We present a paradigm for encoding strain into two dimensional materials (2DM) to create and deterministically place single photon emitters (SPEs) in arbitrary locations with nanometer-scale precision. Our material platform consists of a 2DM placed on top of a deformable polymer film. Upon application of sufficient mechanical stress using an atomic force microscope tip, the 2DM/polymer composite deforms, resulting in formation of highly localized strain fields with excellent control and repeatability. We show that SPEs are created and localized at these nanoindents, and exhibit single photon emission up to 60K. This ***quantum calligraphy*** allows deterministic placement and real time design of arbitrary patterns of SPEs for facile coupling with photonic waveguides, cavities and plasmonic structures. In addition to enabling versatile placement of SPEs, these results present a general methodology for imparting strain into 2DM with nanometer-scale precision, providing an invaluable tool for further investigations and future applications of strain engineering of 2DM and 2DM devices.

Reference: Rosenberger et al., “Quantum Calligraphy: Writing Single-Photon Emitters in a Two-Dimensional Materials Platform,” *ACS Nano*, 2019, https://pubs.acs.org/doi/10.1021/acsnano.8b08730

11:00am **QS+2D+EM+MN+NS+VT-WeM-10 Challenges in Topological and Quantum Materials***, **David Alan Tennant,*** Oak Ridge National Laboratory **INVITED**

Quantum materials are rapidly advancing but still present great challenges. Topological quantum

materials in particular are receiving great attention as they provide potentially robust routes to

quantum information processing that are protected against decoherence processes. Among key

challenges are the prediction and realization of magnetic materials in the form of magnetic Weyl

semimetals and quantum spin liquids as ways of realizing exotic quasiparticles such as Majorana fermions

that can be used for application. These materials present new experimental challenges in terms of identifying their

quasiparticles and demonstrating quantum coherence in their ground states states. Here I will

show how we are using the integrated application of machine learning along with experiment and synthesis

to advance the discovery and understanding of these materials.

11:40am **QS+2D+EM+MN+NS+VT-WeM-12 Rare Earth Silicon Photonics Engineering for Quantum Applications***, A Nandi, X Jiang, D Pak,* Purdue University*; D Perry, E Bielejec,* Sandia National Laboratories*; Y Xuan, **Mahdi Hosseini,*** Purdue University

Controlling intermodal coupling between multiple excitations within a photonic material may enable the design of novel quantum photonic metamaterials exhibiting anomalous effects. Understanding the complex mode dynamics towards the engineering of system Hamiltonian has been the subject of intensive research in recent years. Here, we design an atomic lattice composed of nearly 1000 rare earth ion segments deterministically engineered in silicon photonic structures to modify the emission properties of erbium in silicon. We observe anomalous photon emission at the telecommunication wavelength from atoms geometrically arranged to reduce the propagation loss. Moreover, we map asymmetric emission lineshapes led by intermodal Fano-type interference of the atomic and photonic resonance modes. Our observation paves the way for designing active metamaterials and novel topological photonics with engineered linear and nonlinear interactions for broad applications in quantum information. Moreover, I will result for direct integration of rare earth crystals with silicon photonic chip for implementation of quantum optical memories. The approach can impact the fields of quantum communication and computation through, for example, developing superradiant single photon sources, the study of non-equilibrium many-body quantum dynamics, and engineering quantum transport in a scalable solid-state platform.

2D Materials
Room A216 - Session 2D+EM+MN+NS-WeA
2D Device Physics and Applications

Moderator: Jyoti Katoch, Carnegie Mellon University

2:20pm **2D+EM+MN+NS-WeA-1 Monolayer Electronics and Optoelectronics - Advances, Opportunities and Challenges***, Ali Javey,* University of California at Berkeley **INVITED**

Two-dimensional semiconductors exhibit excellent device characteristics, as well as novel optical, electrical, and optoelectronic characteristics. In this talk, I will present our recent advancements in surface passivation, contact engineering, surface charge transfer doping, and heterostructure devices of layered chalcogenides. We have developed a passivation technique that allows for observation of near-unity photoluminescence quantum yield in monolayer semiconductors. I will discuss the mechanism by which non-radiative recombination can be fully removed in monolayers. The work presents the first demonstration of an optoelectronically perfect monolayer, and highlights one of their unique properties. Finally, I will discuss an AC carrier injection mechanism to enable bright light emitting devices using monolayers, overcoming the problem of Schottky contacts.

3:00pm **2D+EM+MN+NS-WeA-3 Investigation on Graphene Band-gap Engineering for Graphene Transistors Applications***, Benfdila Arezki,* University M. Mammeri Tizi-Ouzou, Algeria

Graphene transistors are considered to be the successor's basic element for the next generation of advanced integrated circuits. However, graphene material suffers from the absence of bandgap to behave as semiconductor. The present paper deals with the investigation on the bandgap engineering approach aiming an increase of the switching characteristics of the graphene transistors.

The main obstacle for graphene transistor is the material zero bandgap that worsens the switching characteristics of the GFETs. Several techniques have been proposed to open a bandgap in graphene, among these engineering techniques, we can cite the Substrate induced bandgap, Bandgap engineering using h-BN/Ni (111). It is known that in theory a maximum of 0.50 to 0.53 eV can be obtained. Such bandgaps are observed on Graphene Bi-Layer (GBL) sheets grown on silicon carbide (SiC).

Other methods are the substitutional doping (SD), Nitrogen doping (NB). In any case graphene engineering should be considered in chemistry and physics view points. A high selective hydrogenation of graphene grown by lithography under the form of nanoruban showed a very interesting result of 0.7 eV. This process is part of selective chemical graphene functionalization techniques (SCGF).

In this paper we will deal with the graphene nanoruban and the opening of a bandgap capable of inducing an appreciable switching current ratio of at least $I_{ON}/I_{OFF}>10^6$.

The Graphene Nano Ribbon (GNR) structure used in the form of GNRFET for logic circuits and RF devices combines the high field, high mobility and the possibility of opening a bandgap. The higher carrier mobility of graphene is the basis of all electrical characteristics of graphene transistors.

In this paper we have used a semi-classical device model including the band to band tunneling that is described in Ref[8] to emphasize on the bandgap engineering. Device performances are studied based on the current-voltage characteristics with respective bandgap width variations. I_{OFF} current estimated and the performance ratio deduced.

3:20pm **2D+EM+MN+NS-WeA-4 Fully Inkjet Printed, High Photo-responsive, 2D WSe_2-Graphene Based Flexible Photodetector***, R Hossain, A Kaul,* ***Avra Bandyopadhyay****,* University of North Texas

Tungsten di-selenide (WSe_2), a classic representative of two dimensional (2D) layered materials has recently drawn much attention due to its unique optoelectronic properties, offering a potential platform to construct hetero-structure photodetector (PD) for ultrafast optoelectronic devices on low-cost, flexible substrates [1,2]. As WSe_2 exhibits a weak van der Waals interlayer bonding, one of the approaches to obtain 2D WSe_2 is through top-down liquid phase exfoliation (LPE), where the bulk crystal is dispersed in a solvent through appropriate sonication and centrifugation conditions [1]. In this work, we report on the synthesis of WSe_2 via LPE and the first-ever assembly of an all inkjet printed WSe_2-graphene hetero-structure PD on flexible polyimide film, where the WSe_2 acted as a photo-active semiconductor and graphene was the carrier collector. The inkjet printed PD was photo-responsive to broadband incoming radiation in the visible regime, and exhibited a high photoresponsivity $R \sim 0.70$ A/W, and detectivity $D \sim 3 \times 10^{10}$ Jones. The strain-dependent measurements were conducted with bending for different curvatures, indicating the feasibility of such devices for large format arrays printed on flexible substrates. The capacitance-frequency (*C-f*) measurements were performed to investigate the trap states. In conclusion, this unique all inkjet printed 2D hetero-junction photodetector formed on flexible and conformable substrate was successfully shown to be highly photo-responsive to a wide range of light intensities and strain levels, making it a promising prospect for scalable flexible electronic and optoelectronic devices and circuitry.

References:

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4:20pm **2D+EM+MN+NS-WeA-7 Chemical Vapor Sensing with Transition Metal Dichalcogenides via Photoluminescence Modulation***,* ***Aubrey T. Hanbicki****, P Campbell, S Sivaram,* U.S. Naval Research Laboratory*; A Kusterbeck,* Nova Research, Inc.*; V Nguyen, A McGill, K McCreary, B Jonker, E Cobas, K Perkins,* U.S. Naval Research Laboratory*; A Friedman,* Laboratory for Physical Sciences

Two-dimensional transition metal dichalcogenides (TMDs) such as MoS_2 and $MoSe_2$ are promising materials for chemical vapor sensing applications. Their potential includes straightforward fabrication, readily available materials, and good selectivity, sensitivity, and speed of response. We previously showed [1] that monolayer TMDs are sensitive to and selective for vapors of strong electron donors and/or strong electron acceptors in concentrations as low as 1 part per million (ppm). Another attractive aspect is that TMDs have been shown to detect chemical vapors and gases in several ways, for instance via changes in electrical conductance or photoluminescence (PL) [2]. Sensors commonly have been fabricated based on the chemiresistive device properties, but here we will discuss our recent studies implementing TMD sensors using the PL as the core element of the sensor. We show that the PL intensity of monolayer CVD-grown WS_2 can rapidly (<< 1sec) detect triethylamine (TEA), a decomposition byproduct of the VX series of nerve agents, in concentrations <<1 ppm. The optical response is similar to the electrical response of other TMDs previously shown [1]. We shall discuss the mechanisms determining the size and shape of the optical responses. We envision suites of different TMDs using both optical and conductance sensing to rapidly and selectively detect chemical agents.

This research was performed while S.V.S held a National Research Council fellowship at NRL. This work was supported by core programs at NRL.

References

[1] A.L. Friedman et al., Sci. Reports 7, 3836 (2017)

[2] P.M. Campbell et al., Appl. Phys. Lett. 113, 163106 (2018)

4:40pm **2D+EM+MN+NS-WeA-8 Effective and Robust Graphene Immunoligical Sensors Functionalized through Non-covalent Ninding of Antibody-Conjugated Tripodal Compound***, A Hugo,* CEA-LETI, France*; C Sun,* Northwestern University*; M Kumar,* CEA-LETI, France*; R Othmen, J Renard, V Bouchiat,* CNRS-Institut Néel, France*; J Mann,* Northwestern University*; J Parpia, H Craighead,* Cornell University*; P Mailley,* CEA-LETI, France*; W Dichtel,* Northwestern University*;* ***Thomas ALAVA****,* CEA-LETI, France

Electrical detection is a very robust technique to transduce the adsorption of charged protein to a biological selective layer (i.e. biosensing). Electrolyte gated field effect transistors (EGFET) integrating graphene monolayers as the transducing element have shown outstanding electrical sensitivity in liquid compared to silicon and diamond based EGFET. In order to build graphene EGFET as effective biosensing unit it is important to attach at its surface a functional layers of biological molecules that will carry the task of enforcing specific detection of compound. Protein are widely used as specific bioreceptor for sensor biological functionalization yet it has been shown that protein lose their function when simply adsorbed on graphene. Covalent binding being out of the way for 2D dimensional crystals such as graphene (for the inherent deterioration of mechanical and electrical properties) we have shown that custom made tripodal compound attaching the graphene basal plane through Pi-stacking of aromatic moieties could be used to attach specific biomolecules to graphene while maintaining their biological function hence their specificity.

In this report we present an optimized fabrication process for graphene EGFET that includes patterning and passivation of electrical contact. The devices reproducibly show state of the art electrical performances. We demonstrate that the process can be simply transferred to different host substrates to integrate graphene EGFET ubiquitously on Silicon, glass or printed circuit board with similar performances. Finally, we implemented biological functionalization of the sensors by attaching streptavidin to the sensor thanks to the non-covalent tripodal compound. We report consistent changes in the Dirac peak of graphene due to the adsorption of tripodal compound and streptavidin as well as the binding of biotin, specifically bound to streptavidin. We show the detection to be specific and reproducible.

5:00pm **2D+EM+MN+NS-WeA-9 Electronic Properties of Ultra-Thin Na$_3$Bi: A Platform for a Topological Transistor*, Mark Edmonds,*** Monash University, Australia **INVITED**

Na$_3$Bi in bulk form represents a zero-bandgap topological Dirac semimetal (TDS), but when confined to few-layers is predicted to be a quantum spin Hall insulator with bulk bandgap of 300 meV.[1] Furthermore, application of an electric field to few-layer Na$_3$Bi has been predicted to induce a topological phase transition from conventional to topological insulator.[2]

I will discuss our efforts to grow epitaxial few-layer Na$_3$Bi via molecular beam epitaxy, and probe its electronic structure and response to an electric field using scanning probe microscopy/spectroscopy and angle-resolved photoelectron spectroscopy. We demonstrate that monolayer and bilayer Na$_3$Bi are wide bandgap quantum spin Hall insulators (E_G>300 meV) that can be tuned with an electric field to semi-metallic, and at higher electric fields re-opened as a conventional insulator.[3] This is the first experimental demonstration of such an electric field tuned topological phase transition in any material. Finally, I will discuss our most recent efforts to perform transport measurements on few-layer Na$_3$Bi at doping levels corresponding to bulk conduction and edge conduction, with and without an applied magnetic field.

References

[1] C. Niu et al., Phys. Rev. B (2017) 95, 075404

[2] H. Pan et al., Scientific Reports (2015) 5, 14639

[3] J. Collins et al., Nature 564, 390 (2018)

5:40pm **2D+EM+MN+NS-WeA-11 Transparent Conductive Oxides in Contact with 2-D Materials*, Ravindra Mehta*, *A Bandyopadhyay, A Kaul,*** University of North Texas

Combining two-dimensional materials with transparent conductive oxide can result in a fully transparent 2D electronics with outstanding device performance. It has been shown that monolayer MoS$_2$ in contact with AZO has 85% transmittance in the visible region, a low threshold voltage (0.69V) and a large switching ratio (4 × 10^8). Another study has shown that using 2D MoS$_2$ as an active channel, tin doped indium oxide as a backgated electrode and zinc doped indium oxide (IZO) as source-drain electrodes, 85% transmittance in the visible region can be obtained. The contact resistance between the IZO and MoS$_2$ was reduced after laser annealing which in turn enhances μ_{eff} and I_{on}/I_{off}. Thus, it becomes essential to study the performance of different transparent conductive oxides in contact with various 2D materials in a transistor. Black phosphorus is an interesting 2D materials since it combines unique attributes of both transition metal dichalcogenides and graphene. CVD is a preferred method compared to other techniques such as mechanical exfoliation, liquid exfoliation, and PVD to synthesize 2D materials since the materials produced are of great quality as is a scalable technique. However, CVD of black phosphorus is challenging. Thus, CVD in addition to exfoliation will be used to develop 2D materials. In this work opto-electronics performance of various transparent conductive oxides in contact with different 2D materials is evaluated with an emphasis on black phosphorus.

6:00pm **2D+EM+MN+NS-WeA-12 Negative Fermi-level Pinning Effect Induced by Graphene Interlayer in Metal/Graphene/Semiconductor Junction**, *H Yoon, W Song,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; S Jung,* SK Hynix, Republic of Korea*; J Kim,* Ulsan National Institute of Science and Technology (UNIST)*; K Mo, G Choi, H Jeong, J Lee, **Kibog Park**,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea

We report the direct observation revealing that the electric dipole layer originating from the off-centric distribution of interacting electrons at metal/graphene interface can induce the negative Fermi-level pinning effect in metal/graphene/semiconductor junction made on a semiconductor substrate containing regions with low interface-trap density. The graphene interlayer takes a role of diffusion barrier preventing the atomic intermixing at interface and preserving the low interface-trap density region. The change of electrostatic potential across the metal/graphene interface due to the interaction dipole layer and the doping of graphene is found to cause the negative Fermi-level pinning effect, supported by the Schottky barrier decreasing as metal work-function increasing. In case of metal/graphene/GaAs junction, the local small patches with very thin or no native oxide layer are considered to be responsible for the negative Fermi-level pinning. In the prevailing region with normal native oxides surrounding the small patches, the Fermi-level pinning appears to be strong. Meanwhile, the negative Fermi-level pinning is found to occur globally in metal/graphene/SiC junction where the SiC substrate is known to produce a low density of interface traps. This work provides an experimental method to form Schottky and Ohmic-like contacts simultaneously on a semiconductor substrate covered partially with graphene by using identical metal electrodes.

Spectroscopic Ellipsometry Focus Topic
Room A212 - Session EL+EM-WeA

Spectroscopic Ellipsometry: Novel Applications and Theoretical Approaches

Moderators: Vanya Darakchieva, Linkoping University, Sweden, Nikolas Podraza, University of Toledo

2:20pm **EL+EM-WeA-1 Optical Hall Effect in the Multi-valley Semiconductor Te-doped GaSb*, Farzin Abadizaman*,** *C Emminger,* New Mexico State University*; S Knight,* University of Nebraska-Lincoln*; M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany*; S Zollner,* New Mexico State University

The authors conducted optical Hall effect (OHE) measurements on Te-doped GaSb (n-type) at room temperature in the far-infrared between 30 cm^{-1} and 700 cm^{-1} at magnetic fields of ±7 T and 0 T. The measurements were performed at an angle of incidence of 45̊ and a resolution of 2 cm^{-1}. The complex dielectric functions and Mueller Matrix (MM) elements were determined from spectroscopic ellipsometry at 0 T in the range of 300 cm^{-1} to 8000 cm^{-1} using an FTIR-VASE ellipsometer and from 30 cm^{-1} to 700 cm^{-1} using the FIR ellipsometer. Using a sum of a Lorentzian oscillator and two Drude terms, the experimental data at zero magnetic field were modeled. From the Lorentzian term, we found the transverse optical (TO) phonon energy at 226 cm^{-1} and the longitudinal optical (LO) phonon energy at 237 cm^{-1}.

Although GaSb is a direct band gap semiconductor, a calculation of the electron concentration indicates that at T = 300 K and a total electron density below 10^{18} cm^{-3}, the majority of carriers are located at the L-valley (67%) while the Γ-valley contains only 33% of the carriers. This implies that in the absence of the magnetic field, two Drude terms are needed to model the data. The surfaces of constant energy at the L-point in the Brillouin zone form eight half-ellipsoids at L, which are characterized by their anisotropic masses. However, due to the symmetry, the valleys at this point are two by two equivalent, which leads to the total number of four valleys. In the absence of a magnetic field, the contribution of all eight half-ellipsoids in the L-valley is reduced to only one Drude term, where the effective mass is the harmonic average of the transverse and longitudinal masses. As the magnetic field is turned on, each ellipsoid contributes to the anisotropic dielectric tensor, which, depending on the effective mass tensor, contributes differently to the total dielectric tensor. Therefore, in the presence of a magnetic field, the data is modeled by the sum of a Lorentzian, a Drude tensor at the Γ-valley and four Drude tensors at the L-valley.

2:40pm **EL+EM-WeA-2 Study of the Temperature-dependent Optical Constants of Noble Metals based on High Temperature Spectroscopic Ellipsometry*, Jiamin Liu*,** *H Jiang, S Liu,* Huazhong University of Science and Technology, China

Noble metals have been widely used in thermo-plasmonics field, such as thermo- photovoltaics, heat-assisted magnetic recording and photothermal therapy, thus studying the temperature-dependent optical constants of these metals are crucial for both understanding the temperature effects on optical properties and providing essential data for the plasmonic simulations.

In this work, a high temperature spectroscopic ellipsometry covering the spectral range of 200-1000nm has been built, which is able to measure the ellipsometric parameters of samples when temperature is varying from 300K to 1200K. The noble metallic samples are heated at a mixing atmosphere of 5% H_2 and 95% Ar to avoid the possible thermal oxidation. An oscillator- parametrization regression method based on the Drude-dual-TaucLorentz-Lorentz model and the B-spline model has been proposed to determine the optical constants and the roughness of the heated noble metals. Both the optical constants and the electronics parameters of noble metals heated below 900K have a temperature-dependency similar to the recently reported results. Taking the gold film as an example, the DC resistivity is increasing from 2.273×10^{-6} to $2.414\times10^{-6}\Omega\cdot$cm with the temperature increasing from 300K to 800K, while the electron relaxation time is decreasing from 20.787 to 9.021fs. Additionally, it has been noticed the first absorption peak near 2.7eV first increases and then decreases, while the second absorption peak near 3.7eV shows the opposite characteristics with the temperature increasing from 300K to 800K. Besides, the optical constants of Au film heated above 900K has some similarities to that of SnTe, which might be caused by the combined effect from the possible formation of Au-Si binary phase and the possible transition of vertical columnar grains to granular grains.

3:00pm **EL+EM-WeA-3 Optical Monitor for the Attitude Tracking using Polarimetry**, ***Song Zhang**, H Gu, H Jiang, S Liu,* Huazhong University of Science and Technology, China

The attitude angles are important parameters describing the motion of the object. In the fields of precision manufacturing, robotics control, navigation of the aircraft, the accurate and real-time measurements of the attitude angles (yaw angle, pitch angle and roll angle) are very important. Due the advantages of non-contact, low cost, non-destructive and high precision, the optical methods have been popular used for measuring the attitude of the object.

In our work, we present a novel optical monitor for the attitude tracking. The proposed method utilizes the principle that polarized light incident in different directions into the birefringent crystals can produce different phase modulations. Then, the attitude angle of the object attached with a birefringent crystal can be obtained by measuring the phase change. The optical monitor is based on the division-of-amplitude polarimetry with a time resolution of several nanoseconds, which is capable of monitoring the changes in all the attitude angles simultaneously. In order to verify the correctness and the performance of the optical monitor, we performed real-time measurement experiments on the attitude angles of a zero-order quarter-wave plate and a multi-order half-wave plate. The roll angle is continuously changed within the range of 0 ~ 360°, while the pitch angle and yaw angle are varied within ±7° and ±40° respectively. The results show that not only the attitude angles, but also the angular velocities and the accelerations of the roll angle, can be extracted, and the errors of all attitude angles is less than 0.5°.

3:20pm **EL+EM-WeA-4 New Progress on the Channeled Spectroscopic Ellipsometry and its Applications**, ***Gai Chin,*** ULVAC Inc., Japan

This presentation describes a novel method for the spectroscopic measurement of the state of polarization of light. A pair of thick birefringent retarders is incorporated into the spectroscopic polarimeter, so the generated channeled spectrum is composed of three quasi-cosinusoidal components carrying the information about the state of polarization of the light that is being measured. Fourier inversion of the channeled spectrum provides the significant parameters for determination of the spectrally resolved Stokes parameters of light. No mechanical movable components for polarization control or active devices for polarization modulation are used, and all the Stokes parameters can be determined at once from only the single spectrum.

The channeled spectroscopic ellipsometry is a snapshot method for the spectrally-resolved polarization analysis. A pair of high-order retarders are utilized to generate a channeled spectrum carrying information about the wavelength-dependent multiple parameters of polarization of light. This method has a feature that it requires no mechanical or active components for polarization-control, such as a rotating compensator and electro-optic modulator.

This novel spectroscopic ellipsometry can measure the thickness and optical constants of thin films at a dramatically fast speed. Its data acquisition time is as short as 10ms. It does not require any active components for polarization-control, such as a rotating compensator or an electro-optical modulator.

It created great opportunities for new applications of the spectroscopic ellipsometry in which the compactness, the simplicity and the rapid response are extremely important. It can be integrated into the deposition tool and successfully measured thin films in-situ and ex-situ. Obviously, those from PVD, CVD and ALD are some promising applications for this novel spectroscopic ellipsometry.

This presentation describes our new progress on some key technologies for enhancing the performance of this channeled spectroscopic ellipsometry by system configuration, data analysis and other creative efforts on developing a series of new high-speed spectroscopic ellipsometers. Some novel applications will be also introduced, such as the PVD, CVD, ALD, EUV, OLED, MEMS and some excellent measurement data of thin films from the semiconductor, flat panel display and other industries.

4:20pm **EL+EM-WeA-7 The Physics of Low Symmetry Metal Oxides: Applications of Ellipsometry**, ***Alyssa Mock,*** U.S. Naval Research Laboratory*; S Knight, M Hilfiker,* University of Nebraska-Lincoln*; V Darakchieva, A Papamichail,* Linkoping University, Sweden*; R Korlacki,* University of Nebraska-Lincoln*; M Tadjer,* U.S. Naval Research Laboratory*; Z Galazka, G Wagner,* Leibniz-Institut für Kristallzüchtung, Germany*; N Blumenschein,* North Carolina State University*; A Kuramata,* Novel Crystal Technology, Inc., Japan*; K Goto, H Murakami, Y Kumagai,* Tokyo University of Agriculture and Technology, Japan*; M Higashiwaki,* National Institute of Information and Communications Technology, Japan*; A Mauze, Y Zhang, J Speck,* University of California Santa Barbara*; M Schubert,* University of Nebraska-Lincoln, Linköping University, Sweden, Leibniz Institute of Polymer Research Dresden, Germany **INVITED**

We discuss the analysis of the dielectric function tensor for monoclinic metal oxides obtained from generalized spectroscopic ellipsometry. We investigate the potential high-power device material gallium oxide and derive dispersions of transverse, longitudinal and plasmon coupled modes [M. Schubert *et al*., Phys. Rev. B 93, 125209 (1-18) (2016); Editors' Suggestion] and the band-to-band transitions and excitons along with their eigenvectors [A. Mock *et al*., Phys. Rev. B 96, 245205 (1-12) (2017)]. Additionally, we show that this technique can fully explain the unusual ordering of optical phonon mode pairs which is observed in beta-Ga2O3 [M. Schubert, A. Mock et al. Phys. Rev. B 99, 041201(R) (2019)] as well as their dependency on free charge carrier concentrations. [M. Schubert, A. Mock et al. Appl. Phys. Lett. 114, 102102 (2019) – Editor's Pick]. We apply this technique also for the identification of transverse and longitudinal phonons in scintillator material cadmium tungstate [A. Mock *et al*., Phys. Rev. B 95, 165202 (1-15) (2017)], and then further extend our methodology for analysis of the dielectric and inverse dielectric tensor for transverse and longitudinal phonon mode dispersion characterization in high-power laser material yttrium orthosilicate [A. Mock *et al*., Phys. Rev. B, 97 165203 (1-17) (2018)].

We apply our technique to investigate the effective electron mass tensor using optical Hall effect measurements [S. Knight, A. Mock *et al*., Appl. Phys. Lett. 112, 012103 (2018); Editors' Pick], the temperature dependence of band-to-band transitions energies [A. Mock *et al*., Appl. Phys. Lett. 112, 041905 (2018)], and the effects of aluminum alloying concentration onto the band-to-band transition energies [M. Hilfiker, A. Mock *et al.* Appl. Phys. Lett. (Under Review)]. We further apply our technique to epitaxial layers of beta-phase gallium oxide and discuss the relationship between the X-ray diffraction measured strains with respect to the optically determined shifts in transverse optical phonon modes as compared to the bulk material. Understanding of the stress and strain relationship to properties in monoclinic materials will help facilitate better control of material properties for engineering next generation power devices based on beta-Ga2O3.

5:00pm **EL+EM-WeA-9 Terahertz Dielectric Anisotropy in Randomly Distributed, Spatially Coherent Polymethacrylate Microwire Arrays Fabricated by Stereolithography**, ***Serang Park,*** University of North Carolina at Charlotte*; Y Li,* University Of North Carolina at Charlotte*; S Lee,* Harris Corp.*; S Schöche, C Herzinger,* J.A. Woollam Co., Inc.*; T Hofmann,* University Of North Carolina at Charlotte

Fabricating terahertz (THz) optical components with tailored dielectric properties including scalable anisotropies via additive manufacturing is drawing substantial interest as it potentially offers a rapid, low-cost pathway for THz optical system development. Metamaterials composed of slanted columnar structures have been reported to exhibit anisotropic behaviors at THz frequencies, which may allow the design of novel optical components including filters and sensors for the THz frequency range. Here, we report on the anisotropic THz-optical response of stereolithographically fabricated polymethacrylate slanted columnar layers. The samples are composed of randomly distributed, spatially coherent polymethacrylate wires with a diameter of 100 µm and a length of 700 µm, which are tilted by 45° with respect to the surface normal of the substrate. Generalized spectroscopic ellipsometry is employed to obtain Mueller matrix spectra of these samples in the range from 210 to 350 GHz. A simple biaxial (orthorhombic) layer homogenization approach is used to analyze the THz Mueller matrix data obtained at different azimuthal orientations. Our observations confirm that randomly distributed, spatially coherent polymethacrylate wire arrays exhibit a strong anisotropic response. In conclusion, stereolithographic fabrication is introduced as an effective tool for fabricating metamaterials with anisotropic THz-optical properties.

5:20pm **EL+EM-WeA-10 Ultrafast Dynamics of Ge, InP and Si Proved by Time-Resolved Ellipsometry***, **Shirly Espinoza**, S Richter, M Rebarz,* Institute of Physics, Academy of Sciences of the Czech Republic, Czechia*; O Herrfurth, R Schmidt,* Universität Leipzig, Felix-Bloch-Institut für Festkörperphysik, Germany*; J Andreasson,* Institute of Physics, Academy of Sciences of the Czech Republic, Czechia*; S Zollner,* New Mexico State University

Recent developments in time-resolved ellipsometry allow us to study the ultrafast behavior of single crystals of undoped Ge, InP and Si at room temperature after carriers have been excited by an ultrashort laser pulse of 1.55 eV. Information about the dynamic processes such as scattering mechanisms of the hot charge carriers and electron-phonon coupling was obtained.

With a resolution of 120 fs, and a time scale from femtoseconds to nanoseconds, the observed changes are bigger in Ge than in the other materials. Our results are in agreement with theoretical and experimental work done some years ago on the dynamics of germanium studied by time-resolved ellipsometry [1,2]. The result of our experiments could go deeper into the details of the dynamics thanks to the development of the time-resolved experimental setup using state of the art technology in the fields of ultrafast lasers, electronics, and optics.

Our current spectral range is from 1.7 to 3.5 eV. The generated carrier density is on the order of $10^{20}\,cm^{-3}$, which allows us to compare the results with published data on doped materials [3].

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5:40pm **EL+EM-WeA-11 Optical Properties of Organic-Inorganic Lead Halide Perovskite Thin Films for Photovoltaics***, **Biwas Subedi**, M Junda, K Ghimire, N Podraza,* University of Toledo

Organic-inorganic lead halide perovskite based photovoltaics (PV) exhibit high initial efficiency, can be solution processed with potentially low material costs, and material band gaps can be tuned by composition. Unfortunately, these perovskites exhibit degradation upon exposure to atmosphere, light, and heat. Spectroscopic ellipsometry over the near infrared to ultraviolet range (0.73-5.9 eV) has been applied to characterize the complex optical response of solution processed ABX_3 (*A*: methylammonium—MA, formamidinium—FA, Cs; *B*: Pb, Sn; *X*: I, Br, Cl) perovskite thin films of different compositions. A parametric optical property model has been developed which includes contributions from electronic transitions above the band gap, the direct band gap, an exponentially decaying Urbach tail, and sub-gap absorption due to defect states. Using this model, above gap critical points, band gap energies, and sub-gap absorption are compared primarily as functions of *A*- and *B*-cation compositions for thin films. In situ, real time spectroscopic ellipsometry (RTSE) of perovskite films undergoing degradation induced by controlled relative humidity is used to track optical properties changes, particularly with respect to sub-gap absorption, and morphology changes occurring at the substrate / film and film / ambient interfaces. These optical property and morphology changes are tracked by RTSE for perovskite thin films of different compositions. Optical properties characterized by spectroscopic ellipsometry are used as input for external quantum efficiency (EQE) simulations of perovskite based PV devices. Comparisons between simulated and measured EQE spectra are used to identify differences in perovskite characteristics arising from the complete solar cell device fabrication process.

6:00pm **EL+EM-WeA-12 Optical Constants of Ni at 300 K from 0.03 to 6.0 eV***, **Stefan Zollner**, F Abadizaman,* New Mexico State University

The optical constants of single-crystalline, polycrystalline, and thin films of Ni from 0.06 to 6 eV are determined from spectroscopic ellipsometry at an angle of incidence of 70̂. The experimental data are analyzed using three alternative methods. In the first method, the dielectric function is written as a sum of Lorentz and Drude oscillators. The second method writes the dielectric function as a product of these oscillators (Kukharskii product). In the third method, a Drude model with frequency dependent scattering rate and plasma frequency is used. We used two Drude terms in the sum model to account for d- and s-electrons. The plasma frequencies were found to be 11.9 eV and 4.86 eV for d- and s-electrons, respectively, leading to a DC conductivity of about 80,000 (1/Ωcm) at 300 K, compared to the electrical DC conductivity of 143,000 (1/Ωcm) reported previously. Furthermore, the model reveals a very large free-electron contribution to the optical constants of Ni, which disproves earlier claims about their insignificance. We also employ graphical techniques to find the plasma frequencies and free-electron scattering rates, which agree well with the parameters found from the first and the second methods.

To prepare clean samples and reduce the thickness of the overlayers, the samples were maintained in ultrahigh vacuum at a temperature of 750 K for 6 hours and then cooled down overnight. A surface roughness thickness of 1-3 nm was found using atomic force microscopy and x-ray reflectivity.

Electronic Materials and Photonics Division
Room A214 - Session EM+2D+NS+TF-WeA

THEME Session: Electronics and Photonics for a Low-Carbon Future

Moderators: Michael A. Filler, Georgia Institute of Technology, Stephen McDonnell, University of Virginia

2:20pm **EM+2D+NS+TF-WeA-1 Uncovering the Materials Paradigm for Solar Absorbers through In situ Imaging and Characterization***, **Mariana Bertoni**,* Arizona State University **INVITED**

The behavior of solar cells is very often limited by inhomogeneously distributed nanoscale defects. This is the case throughout the entire lifecycle of the solar cell, from the distribution of elements and defects during solar cell growth as well as the charge-collection and recombination during operation, to degradation and failure mechanisms due to impurity diffusion, crack formation, and irradiation- and heat-induced cell damage This has been known for a while in the field of crystalline silicon, but inhomogeneities are far more abundant in polycrystalline materials, and are the limiting factor in thin-film solar cells where grain sizes are often on the order of the diffusion length.

We will show that the high penetration of hard X-rays combined with the high sensitivity to elemental distribution, structure, and spatial resolution offers a unique avenue for highly correlative studies at the nanoscale. We will present results on CdTe and $Cu(In,Ga)Se_2$ where carrier collection is directly correlated to the compositional and structural properties of the material under a large variety of synthesis and operating conditions. The segregation of copper at the grain boundaries of both solar absorbers will be discussed in detail as well as the defects impact to carrier collection efficiency. Furthermore, the kinetics of copper segregation during growth and processing will be presented.

3:00pm **EM+2D+NS+TF-WeA-3 Atomic Layer Deposition's Potential in Sustainability***, **Karen Buechler**,* ALD NanoSolutions **INVITED**

Atomic layer deposition (ALD) is an exciting thin film deposition technique which holds the promise to permit enormous material innovations. These material innovations are currently enabling advanced catalysts, high capacity energy storage, advanced manufacturing technologies and many other products. Many of these products work towards reducing energy needs. This talk will highlight several examples of advanced material development through ALD which lead to advanced products which in turn are reducing the carbon footprint of consumers and manufacturers.

4:20pm **EM+2D+NS+TF-WeA-7 Challenges in Materials and Processing to Implementation of Energy Efficient SiC Technology***, **Mei-Chien Lu**,* Monte Rosa Technology

Energy and sustainability have been the main driving forces for the implementation of silicon carbide technology for efficient energy conversion in recent applications in electrical vehicles, hybrid electrical vehicles, data center power management, and photovoltaic and wind power. The decades-long research and development efforts are attributed to the complexity of polytypes of crystal structures of silicon carbide. Reducing these inherent defects from crystal growth and epitaxial layer growth are crucial and continuing tasks. Device architectures are found to be more efficient along selected crystal planes. Innovative processing technologies have to be developed to make these devices built by compound semiconductors with strong covalent bonding manufacturable. Fundamental challenges in materials, devices, and processing technologies will first be briefed. A patent landscape analysis is then conducted herein to reveal the past trends to pave the paths for future research and development. Implementations of silicon carbide devices are in its infancy with some full SiC inverter adopted by a commercial electrical vehicle manufacturer. Market shares and momentum of silicon carbide power electronics as well as the expectations from perspectives of department of energy and industry major players will be discussed. The continuous efforts to address the challenges in materials and processing are encouraged to support the full scale implementation of energy efficient silicon carbide technology.

4:40pm **EM+2D+NS+TF-WeA-8 High Efficiency of Hot Electron Transfer at a Metal-Insulator-Semiconductor to Electrolyte Interface*, Hyun Uk Chae,* ***R Ahsan, Q Lin, R Kapadia,*** University of Southern California

Hot electrons generated from metal has drawn considerable interest in recent years due to the potential for lowering the high-barrier chemical reactions. The majority of hot electron controlling strategy at present have been plasmonic devices using localized surface plasmon resonance (LSPR). Several works have been done using plasmons to induce the hot electron generation to use as catalysts for chemical reactions like hydrogen evolution reaction (HER). However, the efficiency of those devices is extremely low and the mechanism behind it is quite complicated and remain unclear until now. To take advantage of hot electrons efficiently, properly and simply designed devices are required. Here, we demonstrate the different mechanisms of hot electron transfer in a thin gold film in an $Au\text{-}Al_2O_3\text{-}Si$ metal-insulator-semiconductor (MIS) junction by modulating Au film thickness, the applied voltage between Au-Si junction. Hot electron injection contributes to modifying the electron distribution inside the Au electrode, which enables HER to be driven more at same overpotential in solution. This work present that the injection of non-equilibrium electrons can shift the onset voltage of HER by ~0.6 V on the gold film in a 0.5 M H_2SO_4 solution. The efficiency of hot electron density efficiency shows ~85% at 2V of MIS junction bias and solution bias of -1.5 V vs Ag/AgCl is also presented. In addition to experimental results, we carried out the 2-D Monte Carlo simulation to track the injected hot electrons to study for the detail behaviors of thermalization mechanism inside the Au region which indicates the rate of HER. Since electrons quickly lose their energy within femtosecond by electron-electron or electron-phonon scattering, it is significant to see how they behave inside the injected medium to understand the reactions more precisely. The high-efficiency of hot electron usage reported here can be an opening towards the creation of practical hot-electron devices, which could be widely applied to the various fields.

5:00pm **EM+2D+NS+TF-WeA-9 Integrated Photocathodes for Solar Driven Conversion of Carbon Dioxide to value-added Products*, Joel Ager,*** Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

If renewable power sources such as solar and wind could be used to produce chemical precursors and/or fuels, it would provide an alternative to mankind's unsustainable use of fossil fuels and slow the rate of CO_2 emission into the atmosphere [1,2]. Solar to chemical energy conversion by photoelectrochemical processes is a promising approach to address this challenge. Analogous to photovoltaics [3], driving the uphill redox reactions required for net solar to chemical energy conversion necessitates directional charge transport [4]. Additionally, in order to convert carbon dioxide to hydrocarbons, one must manage multi-electron transfer reactions (e.g. 12 in the case of ethylene and ethanol), and minimize potential losses in all parts of the system [5].

Charge selective contacts can be used to steer direct photo-generated carriers to catalytic sites that perform CO_2 reduction in an integrated photocathode. In contrast to conventional photocathode designs which employ p-type absorbers, we used a back illumination geometry with an n-type Si absorber to permit the use of absorbing metallic catalysts which would otherwise block the light. Back and front interfaces were configured by ion implantation and by surface passivation to achieve carrier selectivity. Surface texturing of the Si was used optimize light absorption on the illuminated side and increase the surface area available for catalysis on the electrolyte side. Selectivity to C-C coupled products was achieved by using hierarchical Au- Ag-Cu nanostructures as electrocatalysts [6].

The photovoltage, 550- 600 mV under simulated 1-sun illumination, confirms the carrier selectivity and passivation of the front and back interfaces. Compared to planar controls, textured photocathodes generate higher current densities, exceeding 30 mA cm^{-2}. Under simulated diurnal illumination conditions, over 60% faradaic efficiency to C_{2+} hydrocarbon and oxygenate products (mainly ethylene, ethanol, propanol) is maintained for several days. By coupling photocathodes to series-connected semi-transparent halide perovskite solar cells, we demonstrated stand-alone, CO_2 reduction with a 1.5% conversion efficiency to hydrocarbons and oxygenates [7].

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5:40pm **EM+2D+NS+TF-WeA-11 Modeling of Optical Scattering in White Beetle Scales*, Seung Ho Lee,*** *S Han, S Han,* University of New Mexico

Keywords: Light Scattering; Diffusion Approximation

Abstract: Extremely thin "super-white" coatings that reject solar spectrum but radiate through the transparent atmospheric window in mid-infrared have broad implications in heat management and energy savings for diverse sectors, including building construction, ship manufacturing, and space vehicle operation. In our previous work, we were able to create paint-format "super-white" coatings from microsphere-based materials.[1,2] In this work, however, we borrow our inspiration from white beetles in nature that reveal structural ingenuity at the nanometer scale to achieve such white film. White beetle scales display exceptionally strong light scattering power from a thin anisotropic random biopolymer network. While previous studies have revealed that the anisotropy plays an important role in strong light scattering, the physics of anisotropic light propagation remains less than fully understood. In particular, the studies have shown that light scattering in anisotropic random media may deviate significantly from the anisotropic diffusion approximation. This uncertainty in diffusion approximation led to a study interrogating the scale structures by fully solving Maxwell's equations. These calculations yet left questions on their accuracy, as the structural dimensions in perpendicular direction to the incident light were significantly greater than optical wavelengths. In this work, we systematically reduce the structural size in our simulations, using Fourier analysis of the white beetle scale structures. The size reduction enables fast, accurate calculations of light scattering in the biological structures. From these simulations, we find that the diffusion approximation is valid in describing light propagation in the white beetle scales. Further, we derive a light diffusion equation for anisotropic media from the radiative transfer equation and show that the equation for anisotropic diffusion derived in the past studies is inaccurate. We discuss how our newly derived equation can be used for accurate numerical calculations of light scattering and characterizing anisotropic light diffusion.

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6:00pm **EM+2D+NS+TF-WeA-12 Boosting the Performance of WO_3/n-Si for Photo-electrochemical Water Splitting: From the Role of Si to Interface Engineering**, ***Yihui Zhao,*** Electrochemical Materials and Interfaces (EMI), Dutch Institute for Fundamental Energy Research (DIFFER), The Netherlands*; A Bieberle-Hütter,* Electrochemical Materials and Interfaces (EMI), Dutch Institute for Fundamental Energy Research (DIFFER),The Netherlands, The Netherlands*; G Brocks,* Center for Computational Energy Research, Department of Applied Physics, Eindhoven University of Technology; Computational Materials Science, Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, The Netherla, The Netherlands*; H Genuit,* Dutch Institute for Fundamental Energy Research (DIFFER), The Netherlands*; R Lavrijsen,* Physics of Nanostructures and Center for NanoMaterials (cNM), Department of Applied Physics, Eindhoven University of Technology, The Netherlands

Metal oxide/Si is a promising model for designing high performing electrodes for photo-electrochemical (PEC) water splitting applications. This research provides a fundamental understanding of how and how much the Si contributes to the PEC process in a metal oxide/Si electrode. Applying separated monochromatic UV and IR illumination as well as an Ag interface layer in a WO_3/n-Si heterostructure, we find that the band bending depth in Si, which determines the photovoltage, plays a dominant role. This discovery breaks through the existing design ideas, which focused on facilitating charge transport via interface layers within the Z-scheme, but ignored the resulting changes in the band structure of Si. Based on this discovery, we use a Pt interface layer to enlarge the extent of the n-Si band bending. The resulting WO_3/Pt/n-Si photoelectrodes exhibit a 2 times higher photocurrent density at 1.23 V vs RHE and a 10 times enhancement at 1.6 V vs RHE compared to WO_3/n-Si. In addition, we found that the native SiO_2 layer at the interface prevents Fermi level pinning in the Schottky contact between the Si and the metal. These discoveries should guide future design of metal oxide/Si electrodes for PEC applications.

Thin Films Division
Room A122-123 - Session TF+EM-WeA

Emerging Thin Film Materials: Ultra-wide Bandgap and Phase Change Materials

Moderators: Cary Pint, Vanderbilt University, Brent Sperling, National Institute of Standards and Technology (NIST), Jin-Seong Park, Hanyang University, Korea

2:20pm **TF+EM-WeA-1 MOCVD Growth and Characterization of $ZnGeN_2$-GaN Alloy Films**, ***Benthara Hewage Dinushi Jayatunga****, K Kash,* Case Western Reserve University*; K Reza, H Zhao,* The Ohio State University*; O Ohanaka, R Lalk,* Case Western Reserve University*; M Zhu, J Hwang,* The Ohio State University

$ZnGeN_2$ and GaN are almost lattice matched and both have band gaps of approximately 3.4 eV. A large conduction band offset of ~ 1.4 eV results in a type II band alignment that has great potential for novel device structures. [1,2] For the 50-50 alloy, a slightly positive mixing energy, indicating a tendency toward phase separation, has been predicted. [3] For this mixture the lowest energy configuration is predicted to be an octet-rule-preserving orthorhombic $Pmn2_1$ phase. Other compositions may in principle be made in octet-rule-preserving (and thus lower energy) phases, compared to those that break the octet rule, by random stacking of $ZnGeN_2$ and GaN layers along the orthorhombic *b* axis. [3] Whether random stacking, phase separation, or octet rule violations occur will determine whether, and by how much, the band gap may be tuned with composition, and whether the transport properties are isotropic or anisotropic. The only other work on this alloy reported to date employed a gas reduction nitridation method for synthesis of powders of different compositions, from pure $ZnGeN_2$ to a 50-50 mixture, for photocatalytic applications [4].

Here we report the results of MOCVD growth of this alloy on c-, r-, and a-plane sapphire and c-GaN/sapphire substrates, at temperatures varying from 550 ^{0}C to 700 ^{0}C. Films at the 50-50 composition exhibit better surface morphologies when grown on r-sapphire substrates. Zn incorporation increases with the increase of Ga. The highest growth rate, 3.46 µm/hr, was obtained for a film grown on r-sapphire at 670 ^{0}C and 550 torr, for which a 2θ-ω XRD measurement yielded a wurtzite (110) diffraction peak at 2Ѳ = 57.70^0 with FWHM of 0.76^0 and an RMS surface roughness of ~ 10 nm by AFM. The Hall mobility is 8.19 cm^2/v-s with an n-type carrier concentration of 8.5 x 10^{18} cm^{-3}. Atomic-resolution HAADF-STEM revealed the atomic arrangement of the film near the substrate interface. Introduction of a low-temperature-grown $ZnGeN_2$ buffer layer (480 ^{0}C at 600 torr with low injection of precursors compared to the film growth conditions) led to improved surface morphology and crystal quality, and yielded a room temperature photoluminescence spectrum indicating a band edge at approximately 3.5 eV, close to that predicted for the $Pmn2_1$ phase. [3]

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2:40pm **TF+EM-WeA-2 Device Quality β-Ga2O3 and Related Alloys by MOCVD**, ***Andrei Osinsky****, F Alema,* Agnitron Technology, Inc.*; Y Zhang, A Mauze, J Speck,* University of California, Santa Barbara*; P Mukhopadhyay, W Schoenfeld,* University of Central Florida

We report on the growth of device quality β-Ga_2O_3 and related alloys using MOCVD method. β-Ga_2O_3 thin films are grown using $Ga(DPM)_3$, TEGa and TMGa as Ga sources, and molecular O_2, H_2O vapor, and N_2O as an oxidizer. Films grown from each Ga source had high growth rates with up to 10 ⍰m/hr achieved using TMGa [1]. The effect of the oxidizer identity on the growth rate, electron mobility (μ_e), background carrier concentration, surface and crystalline quality of the films will be discussed. Using pure O_2 as an oxygen source, optimal growth conditions have led to the growth of smooth epitaxial UID Ga_2O_3 thin films with a RT μ_e of 176 cm^2/Vs at n~7x10^{15} 1/cm^3 [2]. The highest μ_e of ~3500 cm^2/Vs has been measured at 54 K. C and H impurities have been shown to be below the SIMS detection limit for a wide range of process conditions, whereby films with n~ 2x10^{14} cm^{-3} were demonstrated. We will also present the growth of device quality β-Ga_2O_3 layers doped with Si, Fe, and N impurities. Critical growth conditions influencing the incorporation of these dopants will be discussed. Using optimum growth conditions, controllable doping with a concentration between 10^{15} and 10^{20} 1/cm^3 were obtained for each dopant. In this work, we will also present on the MOCVD growth of $(Al_x, Ga_{1-x})_2O_3$ alloys. The MOCVD process enables the growth of AlGaO at a temperature >800 ^{o}C, improving the solubility of Al_2O_3 in β-Ga_2O_3 by preventing the formation of volatile suboxides. The MOCVD reactor used in this work has a unique feature that enables it to minimize premature reaction between the species, thereby improving the Al incorporation. AlGaO alloys with Al content of up to 43 % was obtained. The epitaxial growth of high quality strained β-$(Al, Ga)_2O_3/Ga_2O_3$ heterostructures and superlattices will be discussed. The composition homogeneity, structural quality, surface morphology and electrical properties of the heterostructures will be discussed as a function of growth conditions. Finally, the growth of alloys including β-$(In, Ga)_2O_3$ and ZnGaO using MOCVD and their application for photodetection purposes will be discussed.

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3:00pm **TF+EM-WeA-3 Development of the β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 (010) Heterostructures by Plasma-assisted Molecular Beam Epitaxy**, ***James Speck,*** University of California at Santa Barbara **INVITED**

β-Ga_2O_3 is a promising wide bandgap semiconductor for power electronics due to its ~4.8 eV bandgap, reasonable electron mobility, the availability of large area melt grown substrates, and the ability to form heterostructures by alloying on the group III site. In this presentation, we present progress in the plasma-assisted molecular beam epitaxy (PAMBE) growth of β-Ga_2O_3. The presentation will highlight the promise of β-$(Al_xGa_{1-x})_2O_3$/β-Ga_2O_3 heterostructures for lateral devices. We will discuss the growth of β-$(Al_xGa_{1-x})_2O_3$ in the context of the predicted high Al solubility in the β-phase (predicted to be up to ~60-70% for growth temperatures > 800 C). Current experiments limit the Al content to ~25% for coherent growth. We will present detailed analysis of the β-$(Al_xGa_{1-x})_2O_3$ alloys that show the compositions agree between atom probe tomography and high resolution x-ray diffraction. We will highlight a new growth technique, metal oxide catalyzed epitaxy (MOCATAXY), that enables higher growth temperatures due to the addition of an indium catalyst layer that serves both to react with molecular oxygen in the flux and to suppress Ga_2O_3 decomposition via the reaction $Ga_2O_3 \rightarrow Ga_2O + {}^1/_2O_2$. We will demonstrate an increase of growth temperature of ~250 C in comparison to conventional PAMBE growth conditions. We discuss the relative merits and challenges for donor doping in MBE (Si vs. Ge vs. Sn) and options for realizing controllable semi-insulating GaN.

4:20pm **TF+EM-WeA-7 Phase-Change Memory: A Quest from Material Engineering Towards the Device Performances*, Guillaume Bourgeois****,** *G Navarro, M Cyrille, J Garrione, C Sabbione, M Bernard, E Nolot, E Nowak,* CEA-LETI, France **INVITED**

In this paper, we provide some examples of how phase–change material engineering can allow targeting specific memory applications. We present the trade-off in Phase–Change Memory between high-speed performance, required in Storage Class Memory applications, and high thermal stability of the amorphous phase at high temperature, mandatory to address automotive embedded applications.

Phase-Change Memory (PCM) is today the most mature among innovative back-end non-volatile memory technologies, thanks to a wide set of interesting features making PCM technology enough versatile to meet different applications' requirements [1]. A PCM device experiences a physical change of a chalcogenide material sandwiched between two electrodes made possible by the current induced Joule heating flowing through the cell. To achieve the amorphous phase, the PCM in the crystalline phase has to be melted, then rapidly quenched (RESET operation). Thanks to the switching phenomenon, the material in the amorphous phase changes abruptly its conductivity starting to be highly conductive, and can recover the crystalline phase thanks to a specific thermal profile during the pulse application, that provides the energy necessary to the atomic reorganization (SET operation). Thereby, PCM thermal stability relies on the magnitude of the activation energy of the crystallization that results from the combination of crystals nucleation and growth phenomena, on which also the device programming speed relies. Thus, a general trade–off exists between the time required for the SET operation and the device data retention performance [2] (Figure 1). Sb-rich GeSbTe compounds are suitable for high-speed performances with a programming time down to tens of ns still ensuring high endurance and scalability, promising for Storage Class Memory applications (SCM) [3]. Reliability at high temperature is the main requirement to target automotive embedded applications. Ge-rich compositions revealed an endurance of 10^7 cycles up to 175 °C and high temperature data retention compatible with embedded standards. We present here the device performance tuning thanks to the phase–change material stoichiometry engineering (Figure 2). Moreover, we highlight the possibility to boost the PCM performances, such as SET speed and Multi Level Cell capability, thanks to dedicated programming strategies [4].

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5:00pm **TF+EM-WeA-9 Neuromorphic Materials and Architectures for Dynamic Learning and Edge Processing Applications*, Angel Yanguas-Gil,*** Argonne National Laboratory

The ability to dynamically learn and adapt to changes in the environment is one of the hallmarks of biological systems. In the last years there has been a lot of research focused on exploring novel materials, such as those exhibiting memristive behavior, that could enable this type of systems. However, there are comparatively fewer studies focusing on understanding which are the ideal properties that memristive materials should have in order to optimize the performance of architectures capable of dynamic learning. This type of information is crucial to provide design targets for new materials and accelerate the integration of novel devices into architectures optimized for specific applications.

In this work, we identify the subset of the design space of memristive materials that is optimal for dynamic learning applications: in this type of application, a system, in this case a neural network, evolves dynamically and learns as it processes information in real time. This type of behavior is highly desirable for smart sensors or edge processing applications. We have implemented a benchmark architecture consisting of a discrete implementation of spiking neurons where dynamic learning takes place on a set of plastic synapses formed by memristor pairs in a crossbar array. This architecture, which is inspired on the learning center of the insect brain, is capable of dynamically learning standard machine learning datasets such as MNIST and Fashion-MNIST. We have used this model to identify the key properties that memristive materials should have to be optimal dynamic learners, exploring the impact of the kinetics of the memristor's internal state on the system's learning ability, as well as the impact that materials and device variability and errors in tuning the memristor's internal state have on the system's performance.

The results obtained show that a fine degree of control of the memristor internal state is key to achieve high classification accuracy during dynamic learning, but that, within this optimal region, learning is extremely robust to both device variability and to errors in the writing of the internal state, in all cases allowing for 2σ variations greater than 40% without significant loss of accuracy. Moreover, the dynamics of the internal state can show distinct kinetics depending on the polarity, something that is critical for bipolar memristors. These criteria are significantly different from those required for ReRAM applications or even for neuromorphic applications based on offchip training, where the robustness of reading and writing operations are critical.

5:20pm **TF+EM-WeA-10 Atomic Layer Deposited VO_2 Thin Films Towards Modulated Infrared Optoelectronic Devices*, Virginia Wheeler,*** *C Ellis, M Currie, J Avila, M Meeker, A Giles,* U.S. Naval Research Laboratory*; J Caldwell,* Vanderbilt University*; J Tischler,* U.S. Naval Research Laboratory

VO_2 is a phase change material that undergoes a first order crystalline phase transition at a critical temperature (T_c = 68°C), resulting in significant changes in intrinsic electrical and optical properties, especially in the infrared. Optical changes with this phase transition are of particular interest as passive and active components of optoelectronic devices, specifically for thermal regulation and modulated signaling. Realizing this type of device often requires the integration of thin, conformal VO_2 films with complex, non-planar structures (like metamaterials). Thus, atomic layer deposition (ALD) is the ideal deposition method in these cases.

Traditional metal-based plasmonic materials suffer from high optical losses, which has promoted research towards alternative low-loss materials that can support plasmonic-like effects. One such approach employs phonon-mediated collective-charge oscillations (surface phonon polaritons, SPhPs) that are supported by nanostructured polar dielectric materials (SiC, AlN, etc), which inherently are low-loss. Geometric design of the nanostructures enables spectral tuning of resonant features between the longitudinal and tranverse optical phonons of the polar material, typically in the infrared regions. However, the spectral position and amplitude of these resonances remain fixed after fabrication. Integrating phase change materials with these structures provides a way to achieve active modulation of resonances.

In this work, nanopillar arrays were etched into SiC and AlN to create narrowband resonances in the long-wave infrared region. These structures were subsequently coated with ALD VO_2 films with different thicknesses (8-75nm). As-deposited VO_2 films are highly conformal and amorphous, and cause the resonances to shift and broaden due to the different dielectric environment. However, after annealing the films at 525°C in $6x10^{-5}$ Torr, the VO_2 films crystallize resulting in sharper resonances and spectral locations close to the initial uncoated structures. Temperature-dependence reflectance and emission measurements show that by heating through the VO_2 transition temperature, the amplitude of the resonances can be modulated. Full signal modulation (ie. on/off) requires at least a 16nm VO_2 film. This work shows the ability to actively tune surface phonon polariton resonances using ALD phase change materials.

5:40pm **TF+EM-WeA-11 Deposition Process for Vanadium Dioxide Thin Films for RF Applications*, Mark Lust,*** *S Chen, N Ghalichechian,* The Ohio State University

Phase change materials (PCM) are attractive due their tunability, wide range of applications, and quasi-passive actuation as compared to traditional active integrated circuits. Vanadium dioxide (VO_2) is particularly appealing because of its high contrast between dielectric and conductive states and the relatively low temperature (68 °C) at which its metal-insulator transition (MIT) occurs. This work details a process for depositing high quality VO_2 thin films on C-plane sapphire wafers as well as alumina (Al_2O_3) buffer layers using atomic layer deposition (ALD) on silicon substrates. We compare resistivity vs. temperature measurements of VO_2 on sapphire with VO_2 on the Al_2O_3 buffer layers both as-deposited and after rapid thermal annealing (RTA) at temperatures ranging from 950 to 1150°C. The VO_2 thin films yielded ratios of resistivity between conductor (heated) and dielectric (room temperature) states of 9.8×10^4 Ω-cm, 5.2×10^3 Ω-cm, and 1.5×10^4 Ω-cm when deposited on crystalline sapphire, amorphous Al_2O_3 buffer layers, and annealed Al_2O_3 buffer layers, respectively. This corresponds to an improvement by a factor of 2.9 in the annealed buffer layers over the amorphous buffer layers. Moreover, we studied various VO_2 thin films using X-ray diffraction, which showed clear indications that the films are highly pure and have a preferred crystal orientation. The deposition process we have developed will allow us to use high quality VO_2 thin films on silicon substrates, especially millimeter-wave devices such as reconfigurable antennas, sensors, and meta-surfaces.

6:00pm **TF+EM-WeA-12 Low Power, Microwave Solid State Oscillators Based on Phase Change Materials***, **Yang Liu**, Z Du, B Zhao, H Wang, J Ravichandran,* University of Southern California

The information age has unleashed an exponential growth in access and quality of life for human beings, but sustaining this growth is key to our future. Currently, 10% of the world's energy is consumed for processing, communication or storage of digital media and this share is constantly increasing, which is a slowly unfolding energy crisis.[1] With the growing need for artificial intelligence, efficient use of energy for computing warrants a departure from digital logic. Brain-inspired neuromorphic computing is envisioned to be several times more efficient for associative learning problems. Phase change materials demonstrating metal to insulator transitions are suitable to realize solid state neurons in this neuromorphic framework. VO_2 undergoes a 5 order-of-magnitude change in resistivity near room temperature with minimal structural change.[2] We designed highly energy efficient, low power oscillators based on $VO_2/SrRuO_3$ heterostructures in the light of thermal engineering. Early simulation work has demonstrated low power consumption down to 45 µW with 3 GHz driving frequency.[3] High-quality epitaxial VO_2 thin films have been deposited on various *3m* surface symmetry substrate, $SrTiO_3$ and $[LaAlO_3]_{0.3}[Sr_2AlTaO_6]_{0.7}$.[4] VO_2 thin films have shown sharp 4 orders of magnitude change in resistivity around the transition temperature. The thermal boundary conductance is measured by time-domain thermoreflectance. We also present our experimental effort to achieve energy efficient and low power oscillators for neuromorphic computing.

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2D Materials

Room A216 - Session 2D+EM+MI+NS+QS+SS-ThM

Dopants, Defects, and Interfaces in 2D Materials

Moderator: Evan Reed, Stanford University

8:00am **2D+EM+MI+NS+QS+SS-ThM-1 Interfacial Engineering of Chemically Reactive Two-Dimensional Materials***, **Mark Hersam**,* Northwestern University **INVITED**

Following the success of ambient-stable two-dimensional (2D) materials such as graphene and hexagonal boron nitride, new classes of chemically reactive layered solids are being explored since their unique properties hold promise for improved device performance [1]. For example, chemically reactive 2D semiconductors (e.g., black phosphorus (BP) and indium selenide (InSe)) have shown enhanced field-effect mobilities under controlled conditions that minimize ambient degradation [2]. In addition, 2D boron (i.e., borophene) is an anisotropic metal with a diverse range of theoretically predicted phenomena including confined plasmons, charge density waves, and superconductivity [3], although its high chemical reactivity has limited experimental studies to inert ultrahigh vacuum conditions [4-7]. Therefore, to fully study and exploit the vast majority of 2D materials, methods for mitigating or exploiting their relatively high chemical reactivity are required [8]. In particular, covalent organic functionalization of BP minimizes ambient degradation, provides charge transfer doping, and enhances field-effect mobility [9]. In contrast, noncovalent organic functionalization of borophene leads to the spontaneous formation of electronically abrupt lateral organic-borophene heterostructures [10]. By combining organic and inorganic encapsulation strategies, even highly chemically reactive 2D materials (e.g., InSe) can be studied and utilized in ambient conditions [11].

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8:40am **2D+EM+MI+NS+QS+SS-ThM-3 Effects of Mn Doping on the Surface Electronic Band Structure and Bulk Magnetic Properties of ZnS and CdS Quantum Dot Thin Films***, **Thilini K. Ekanayaka**[1], G Gurung,* University of Nebraska-Lincoln*; G Rimal,* Rutgers University*; S Horoz,* Siirt University, Turkey*; J Tang, T Chien,* University of Wyoming*; T Paudel, A Yost,* University of Nebraska-Lincoln

Semiconducting quantum dots (QDs) are desirable for solar cells due to the ability to tune the band gap by changing the QD size without changing the underlying material or synthesis technique. Doping QDs with a transition metal is one way of further tailoring the electronic band structure and magnetic properties of QDs in order to improve overall device performance. Understanding the mechanisms causing the change in the electronic band structure and magnetic properties due to transition metal doping is important to device-by-design schemes. In this study, we measure the effects of Mn dopants on the surface electronic band structure of ZnS and CdS QDs using scanning tunneling microscopy/spectroscopy and photoemission spectroscopy. In both the ZnS and CdS systems, a decrease in band gap upon introduction of Mn is observed. Additionally, a rigid band shift was observed in ZnS upon Mn doping It is argued, using X-ray photoemission spectroscopy, that the rigid band shift is due to a hole-doping mechanism caused by the formation of Zn vacancies accompanied by a Mn^{3+}oxidation state which leads to the reduction in total S vacancies as compared to the undoped ZnS system. No band shift was observed in CdS upon Mn doping, but a strong sp-d hybridization takes place which results in a significant band gap reduction. Furthermore, induced midgap states originating from the Mn dopant appear in the surface electronic band structure of Mn: CdS. Measurements of the magnetization of Mn doped and undoped ZnS and CdS confirms the presence of d^0 ferromagnetism. The magnetization is reduced and the coercive field is increased post Mn doping which suggests the anti-ferromagnetic alignment of Mn dopant atoms. Density Functional Theory calculations support the Mn anti-ferromagnetic alignment hypothesis and a ground state with Mn in the 3^+ valence. This study provides important information on the role of dopants and vacancies in dilute magnetic semiconductor quantum dot materials for applications in photovoltaics and spintronics.

9:00am **2D+EM+MI+NS+QS+SS-ThM-4 Interaction of Molecular O_2 with Organolead Halide Nanorods by Single-Particle Fluorescence Microscopy***, **Juvinch Vicente**, J Chen,* Ohio University

The photoluminescence (PL) of organolead halide perovskites (OHPs) is sensitive to its surface conditions, especially surface defect states, making the PL of small OHP crystals an effective way to report their surface states. At the ensemble level, when averaging a lot of nanocrystals, the photoexcitation of OHP nanorods under inert nitrogen (N_2) atmosphere leads to PL decline, while subsequent exposure to oxygen (O_2) results to reversible PL recovery. At the single-particle level, individual OHP nanorods photoblinks, whose probability is dependent on both the excitation intensity and the O_2 concentration. Combining the two sets of information, we are able to quantitatively evaluate the interaction between a single surface defect and a single O_2 molecule using a kinetic model. This model provides fundamental insights that could help reconcile the contradicting views on the interactions of molecular O_2 with OHP materials and help design a suitable OHP interface for a variety of applications in photovoltaics and optoelectronics.

9:20am **2D+EM+MI+NS+QS+SS-ThM-5 Complementary Growth of 2D Transition Metal Dichalcogenide Semiconductors on Metal Oxide Interfaces***, T Wickramasinghe, **Gregory Jensen**, R Thorat,* Nanoscale and Quantum Phenomena Institute*; S Aleithan,* Nanoscale and Quantum Phenomena Institute, Saudi Arabia*; S Khadka, E Stinaff,* Nanoscale and Quantum Phenomena Institute

A chemical vapor deposition (CVD) growth model will be presented for a technique resulting in naturally formed 2D transition metal dichalcogenide (TMD) based metal-oxide-semiconductor structures. The process is based on a standard CVD reaction involving a chalcogen and transition metal oxide-based precursor. Here however, a thin metal oxide layer, formed on lithographically defined regions of a pure bulk transition metal, serves as the precursor. X-ray diffraction and cross -sectional SEM studies show insight into the type and thickness of the metal oxide created during optimal growth conditions. The chalcogen reacts with the metal oxide, forming TMD material which migrates outward along the substrate, leading to lateral growth of highly-crystalline, mono-to-few layer, films. In addition to displaying strong luminescence, monolayer Raman signatures, and relatively large crystal domains, the material grows deterministically and selectively over large regions and remains connected to the bulk metallic patterns, offering a scalable path for producing as-grown two-dimensional materials-based devices.

9:40am **2D+EM+MI+NS+QS+SS-ThM-6 Kagome-type Lattice Instability and Insulator-metal Transition in an Alkali-doped Mott Insulator on Si(111)***, **Tyler Smith**, H Weitering,* University of Tennessee Knoxville

The 1/3 ML monolayer (ML) 'alpha phase' of Sn on Si(111) is a remarkable platform for the study of strong correlations in a spin ½ triangular adatom lattice. In this work, we employ an adatom doping scheme by depositing potassium onto the triangular Sn lattice. The K-atoms destabilize the parent Mott insulating phase and produce a charge-ordered insulator, revealing a rare Kagome lattice at the surface. Scanning Tunneling Microscopy and Spectroscopy reveal a phase transition from an insulating kagome lattice to a metallic triangular lattice at about 200 K. DFT band structure calculations for this kagome system [J. Ortega et al., unpublished] reveal the presence of a flat-band just below the Fermi level, making this novel system a compelling platform for hole-doping studies of magnetic and/or superconducting instabilities.

11:00am **2D+EM+MI+NS+QS+SS-ThM-10 Chemical Migration and Dipole Formation at TMD/TI Interfaces***, **Brenton Noesges**, T Zhu,* The Ohio State University*; D O'Hara,* University of California, Riverside*; R Kawakami, L Brillson,* The Ohio State University

Proximity effects at the interface between two materials can induce physical properties not present in either material alone. Topological insulators (TIs) such as Bi_2Se_3 with non-trivial surface states are sensitive to interface proximity effects where overlayers and adsorbates can act as a dopant source, chemically interact with the TI surface, or couple across the

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[1] **National Student Award Finalist**

TI surface states leading to novel quantum phases. Transition metal dichalcogenides (TMDs), a class of 2D van der Waals materials, are a promising candidate to control this interface given the shared general hexagonal symmetry and wide range of TMD properties. However, the interface between TMDs and Bi_2Se_3 can be more complex than the ideal van der Waals interface. Chemical species exchange like metal cation exchange and selenium migration from substrate to growing film can impact the structure and properties of either layer. Self-assembly mechanisms have also been observed where complete metal monolayers form inside the Bi_2Se_3 quintuple layer [1]. We used x-ray photoelectron spectroscopy (XPS) connected in vacuo via UHV suitcase to a molecular beam epitaxy (MBE) system to investigate chemical interaction at the interface between selenide TMDs and Bi_2Se_3. Air-free transferring is crucial to minimize contamination at the interface and prevent oxidation in the air-sensitive TMDs. We compare the effects of ultrathin pure Mn metal overlayers and monolayer $MnSe_x$ on Bi_2Se_3 to pristine Bi_2Se_3. In the case of pure Mn metal on Bi_2Se_3, Bi core levels exhibit a 1.7 eV shift toward lower binding energies while the Mn core levels also show signs of Mn-Se bonding. These core level changes indicate that, in the absence of excess Se during growth, Mn pulls Se from the substrate leaving behind Bi_2 bilayers near the surface. Depositing a monolayer of $MnSe_x$ produces very different results than the pure metal case. Bi_2Se_3 core levels measured below the monolayer $MnSe_x$ film exhibit a rigid 0.8 eV chemical shift toward higher binding energies indicative of surface/interface dipole formation. The presence of this dipole is likely due to growth of primarily α-MnSe instead of the 1T-$MnSe_2$ 2D phase [2]. Scanning tunneling microscopy (STM) height maps and spectroscopy data provide further evidence of majority α-MnSe formation. XPS core level analysis combined with controlled depositions, air-free transfers and surface analysis can provide a consistent explanation of chemical diffusion and dipole formation at a TMD/TI interface. This work is supported by NSF MRSEC under award number DMR-1420451.

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11:20am **2D+EM+MI+NS+QS+SS-ThM-11 Atomically Resolved Electronic Properties of Defects in the in-plane Anisotropic Lattice of ReS_2*, Adina Luican-Mayer,*** University of Ottawa, Canada

Among the layered transition metal dichalcogenides, the compounds that exhibit in-plane anisotropy are of particular interest as they offer an additional tuning knob for their novel properties. In this talk, we present experimental evidence of the lattice structure and properties of semiconducting ReS_2 by using scanning tunneling microscopy and spectroscopy (STM/STS). We demonstrate that rhenium atoms form diamond-shaped clusters, organized in disjointed chains and characterize the semiconducting electronic band gap by STS. When imaging the surface of ReS_2, we encounter "bright" or "dark" regions indicating the presence of charged defects that will electrostatically interact with their environment. By spatially mapping the local density of states around these defects, we explore their origin and electrostatic nature. Experimental results are compared with ab-initio theory.

11:40am **2D+EM+MI+NS+QS+SS-ThM-12 Charge Diminishing at the Si-SiO_2 System and its Influence on the Interface Properties*, Daniel Kropman,*** *V Seeman,* Tartu University, Estonia*; A Medvids, P Onufrievs,* Riga Technical University, Latvia

The fact that a positive charge formation occurs in SiO_2 film during the process of Si thermal oxidation is already known, with the formation being dependent upon the oxidation conditions which involve temperature, time, and ambient conditions. This is connected by oxygen vacancies in the SiO_2 film and unsaturated $Si^{3\bullet}$ bonds at the interface. Until now this process has not been studied in depth at an atomic level. The purpose of the present work is to investigate the charge formation in the Si-SiO_2 system and its diminishing by means of the appropriate choice of oxidation conditions via EPR spectroscopy, IR spectroscopy, CV curves, TEM, and deflection measurements. Laser irradiation and ultrasonic treatment were used for the modification of interface properties. It has been established that, at an oxidation temperature that is within the range of 1125^0C-1130^0C in SiO2 film with a thickness of 0.2-0.3μ at the interface, there appears a low positive or negative charge which is connected with negatively charged acceptors that are formed by Si vacancies, and the positive charge in the SiO_2 is compensated. The results that were obtained coincide with the point defects generation kinetic model in the Si-SiO_2 system which was proposed in [1] and was confirmed experimentally [2]. Integral circuit technology conditions that allow the interface charge to diminish were introduced by the semiconductor plant, ALFA (Riga, Latvia) [3]. We supposed that these results, which were obtained during long term collaboration between Estonia and Latvia, constituted a discovery that had been achieved by Si-SiO_2 system investigation no less than thirty years ago: the discovery of the quantum Hall effect on the Si-SiO2 structure [4].

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12:00pm **2D+EM+MI+NS+QS+SS-ThM-13 Size-independent "Squeezed" Shape of Metal Clusters Embedded Beneath Layered Materials***, A Lii-Rosales,* Ames Laboratory and Iowa State University*; S Julien, K Wan,* Northeastern University*; Y Han,* Ames Laboratory and Iowa State University*; K Lai,* Iowa State University*; M Tringides, J Evans,* ***Patricia A. Thiel,*** Ames Laboratory and Iowa State University

We have developed a continuum elasticity model for metals embedded beneath the surfaces of layered materials. The model predicts that the equilibrated cluster shape is invariant with size, manifest both by constant side slope and by constant aspect ratio (width:height ratio). This prediction is rationalized by dimensional analysis of the relevant energetic contributions. The model is consistent with experimental data for Cu and Fe clusters embedded in graphite, especially in the limit of large clusters. For comparison, we have performed a Winterbottom analysis of the equilibrium shape of an uncovered Cu cluster supported on top of graphite. The aspect ratio of the embedded cluster is about an order of magnitude higher than that of the supported cluster. Analysis of key energetics indicates that this is due to the strain energy (resistance to deformation) of the top graphene membrane, which effectively squeezes the metal cluster and forces it to adopt a relatively low, flattened shape. These insights may be useful for developing components such as metallic heat sinks or electrodes in electronic devices that use two-dimensional or layered materials.

Electronic Materials and Photonics Division
Room A214 - Session EM+AP+MS+NS+TF-ThM

Advanced Processes for Interconnects and Devices

Moderators: Andy Antonelli, Nanometrics, Bryan Wiggins, Intel Corporation

8:00am **EM+AP+MS+NS+TF-ThM-1 High-density Plasma for Soft Etching of Noble Metals*, Gerhard Franz,*** *V Sushkov,* Munich University of Applied Sciences, Germany*; W Oberhausen, R Meyer,* Technische Universität München, Germany

During our research to define a contact which can be serve as thin hard mask in III/V semiconductor processing, we focused on the Bell contact which consists of Ti/Pt(Mo)/Au and chlorine-based plasmas generated by electron cyclotron resonance. For platinum, we identified PF_3 as main component which acts comparable to CO [1]. This fact triggered our search for suited etchants for gold and copper. For Au, the best ambient is a mixture of CH_4, Cl_2, and O_2 which is stabilized by Ar [2]. This mixture generates residual-free etching of metal films which are clearly free of "fencing" and "hear's ears."

The etching process has been established up to thicknesses of half a micron which is the typical thickness of metal films on the p-side of laser devices. With the aid of optical emission spectroscopy, the generation of CO could be proven [3]. This reagent seems to be the main component for real etching without residual fencing.

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8:20am **EM+AP+MS+NS+TF-ThM-2 Crystalline InP Growth and Device Fabrication Directly on Amorphous Dielectrics at Temperatures below 400°C for Future 3D Integrated Circuits*, Debarghya Sarkar,*** *Y Xu, S Weng, R Kapadia,* University of Southern California

A fundamental requirement to realize 3D integrated circuits is the ability to integrate single crystal semiconductor devices on the back-end of functional layers within a thermal budget of ~400 °C. Present state-of-the-art methods involve wafer bonding or epitaxial growth and transfer, since directly growing on amorphous materials by traditional epitaxial growth processes like MOCVD and MBE would give polycrystalline films with submicron-scale grains. To that end, a newly introduced and actively developing growth method called Templated Liquid Phase (TLP) has demonstrated the ability to achieve single crystal compound semiconductor mesas of areal dimension ~ 10um diameter on diverse amorphous substrates. While previous demonstrations of TLP growth were at temperatures around 500-600 °C, in this presentation we would discuss some of the recent material characteristics and device results achieved and insights obtained, for crystalline InP mesas grown on amorphous dielectrics at temperatures below 400 °C. InP nucleation and growth was obtained for temperatures 360 °C down to 200 °C. Morphological variations of the grown crystals observed under different growth conditions (temperature, pressure, precursor flux) and strategies to obtain compact macro-defect free crystal growth would be presented. Contrary to general expectation of poor optoelectronic quality at these lower temperatures, the room temperature steady-state photoluminescence shows peak position and full width at half maximum comparable to that of commercial InP wafer. External quantum efficiency is within an order of magnitude of single crystal commercial wafer at optimal growth conditions. Back-gated phototransistor was fabricated using low temperature InP grown directly on the amorphous gate oxide, and with all processing steps below the thermal budget of 400 °C. A typical device showed reasonable ON-OFF ratio of about 3 orders of magnitude, with peak responsivity of 20 A/W at V_{gs}=3.2V and V_{ds}=2.1V under an irradiance of 4 mW/cm^2 of broadband light. In summary, this technology could potentially open up a viable avenue to realize 3D integrated circuits by enabling integration of high performance electronic and optoelectronic devices on the back-end of functional layers within the acceptable thermal budget of 400^{0}C.

8:40am **EM+AP+MS+NS+TF-ThM-3 The Role and Requirements of Selective Deposition in Advanced Patterning***, **Charles Wallace**,* Intel Corporation **INVITED**

The edge placement error (EPE) margin on features patterned at tight pitches presents a difficult integrated challenge. Area selective deposition, chemically selective etches and the design of thin films for selectivity have risen to the top priorities in advanced patterning. The EPE control requirement creates a complex interaction between many integrated modules such as thin film deposition, etch (wet and dry), chemical-mechanical polish and lithography. The introduction of EUV lithography into the semiconductor patterning process has enabled some simplification of process architecture; however, has not decreased EPE margin enough to keep up with the pitch scaling requirements. Chemical selectivity is the most effective way to avoid EPE-caused failures on devices which lead to poor yield. Some of the limits to achieving selective growth solutions include development of self-assembled monolayers (SAMs), selective ALD/CVD growth and the metrology required to prove success. The development of manufacturable deposition chambers by the industry is a key requirement in order to adequately test the capability of these new process options.

9:20am **EM+AP+MS+NS+TF-ThM-5 Graphene-Template Assisted Selective Epitaxy (G-TASE) of Group IV Semiconductors***, **M. Arslan Shehzad**, A T. Mohabir, M Filler,* Georgia Institute of Technology

As conventional 2-D transistor scaling approaches its limits, 3-D architectures promise to increase the number of devices and reduce interconnect congestion. A process able to monolithically integrate single-crystalline group IV materials into the back-end-of-line (BEOL) may enable such designs. Here, we demonstrate the graphene-template assisted selective epitaxy (G-TASE) of single-crystal Ge on amorphous substrates at temperatures as low as 250 ˚C. This work represents a significant step forward for TASE methods, which have been largely limited to III-V and II-VI materials, bulk crystal templates, as well as higher temperatures. We specifically grow Ge nanostructures on graphene-on-oxide at the bottom of nanometer-scale oxide trenches by leveraging differences in group IV atom sticking probability between graphene and oxide surfaces. Raman mapping confirms the single crystallinity of as-grown Ge crystals. Time-dependent studies show a linear increase in Ge crystal height even after emerging from the oxide trench, indicating Ge atoms preferentially adsorb to the top facet under our growth conditions. Our studies also reveal that G-TASE is sensitive to the plasma process used to expose graphene in the oxide trenches. This work extends TASE to a new, technologically-relevant materials system and provides fundamental insight into the underlying physicochemistry.

KEY WORDS: silicon, germanium, epitaxy, graphene, selective deposition

9:40am **EM+AP+MS+NS+TF-ThM-6 Resistivity and Surface Scattering Specularity at (0001) Ru/dielectric Interfaces***, S Ezzat,* University of Central Florida*; P Mani,* View Dynamic Glass, Inc.*; A Khaniya, W Kaden,* University of Central Florida*; D Gall,* Rensselaer Polytechnic Institute*; K Barmak,* Columbia University*; **Kevin Coffey**,* University of Central Florida

In this work we report the variation of resistivity with film thickness and with changes in surface characteristics for ex-situ annealed single crystal (0001) Ru thin films grown on c-axis sapphire single crystal substrates. The room temperature deposition of SiO_2 on the Ru surface increased the resistivity of the annealed films and is interpreted as an increase in diffuse scattering of the upper surface from a primarily specular previous condition in the context of the Fuchs-Sondheimer model of surface scattering. The characterization of the films and upper Ru surface by low energy electron diffraction (prior to SiO_2 deposition), x-ray reflectivity, x-ray diffraction, and sheet resistance measurements is reported. The film resistivity and specularity of the Ru/SiO_2 interface is observed to reversibly transition between high resistivity (low specularity) and low resistivity (high specularity) states.

11:00am **EM+AP+MS+NS+TF-ThM-10 Electrochemical Atomic Layer Deposition and Etching of Metals for Atomically-Precise Fabrication of Semiconductor Interconnects***, Y Gong, K Venkatraman, **Rohan Akolkar**,* Case Western Reserve University **INVITED**

Moore's law drives continued device miniaturization in nano-electronics circuits. As critical dimensions are approaching the single nanometer length scale, the semiconductor industry is seeking novel technologies for precisely tailoring materials and structures at the atomic scale. While vapor-phase, plasma-assisted techniques of atomic layer deposition (ALD) and etching (ALE) are capable of providing nano-scale control over metal deposition and etching, these processes may not provide the requisite atomic-scale precision. Additionally, ALD precursors are unstable and often expensive. Thus, alternative solution-phase electrochemical processes are being developed in our laboratory. In our electrochemical ALD (e-ALD) approach, a sacrificial monolayer of zinc is first deposited on the noble substrate via underpotential deposition (UPD). The zinc adlayer then undergoes spontaneous surface-limited redox replacement (SLRR) by the desired metal such as Cu or Co. Sequential UPD and SLRR steps enable fabrication of multi-layered deposits in a layer-by-layer fashion. An analogous approach for electrochemical ALE (e-ALE) is also being developed. In electrochemical ALE of Cu, surface-limited sulfidization of Cu forms a cuprous sulfide (Cu_2S) monolayer. The sulfidized Cu monolayer is then selectively removed through spontaneous complexation of the Cu^{+1} in a chloride-containing etchant medium. The sequence can be repeated to etch bulk metal films one atomic layer at a time. This talk will highlight numerous advantages and fundamental characteristics of e-ALD and e-ALE processes and describe opportunities for integrating them in wafer-scale metallization applications.

11:40am **EM+AP+MS+NS+TF-ThM-12 Mechanical Properties of Patterned low-κ Films Measured by Brillouin Light Scattering***, **Jon Zizka**, H Wijesinghe,* The Ohio State University*; S King, H Yoo,* Intel Corporation, USA*; R Sooryakumar,* The Ohio State University

In order to improve device performance of interconnects, the microelectronics industry utilizes low- κ dielectric technology in place of traditional SiO_2. Integration of these materials into circuits has, however, been challenging due to poor mechanical stability as a result of the increased dielectric porosity. Large thermal stresses may also build up during successive thermal cycling due to differences in the thermal expansion of component materials. These adverse features become more prominent as smaller dimensions are sought for improvement in device performance. While titanium nitride (TiN) is currently being widely used as a hard mask to pattern low- κ materials such as SiOC:H into desired architectures with < 100 nm length scales, the high stress and stiffness of the TiN over-layer can influence the delicate underlying patterns and affect device performance.

In this study we utilize Brillouin light scattering (BLS) to probe the elastic properties of TiN/SiOC:H structures grown on Si that have been patterned into a series of parallel wires of rectangular cross-sections with sub 200 nm pitch and depths. In studying the influence of the hard mask on the mechanical properties of SiOC:H, BLS offers a non-invasive approach to detect thermally activated acoustic excitations and to measure their mode dispersions for incident light with wave-vector components parallel or perpendicular to the TiN wires. The widely-used technique of nanoindentation (NI) to measure mechanical properties has been shown, for ultra-thin soft films, to interact with the underlying substrate, thus skewing the results. On the other hand, the inelastic light scattering approach probes ambient modes allowing for the individual acoustic behavior of the film to be distinguished from the substrate.

The results of measurements performed on samples with a range of wire dimensions (width/depth) will be presented that include the dependence of the Brillouin peak intensities on the incident and scattered light polarization as well as a model of the mode profiles. The latter include finite element modeling that simulate the different mode frequencies and associated relative vertical and horizontal displacements for the non-dispersive cantilever type modes that characterize modes with wave-vector perpendicular to the TiN wires. The modes with wave-vector parallel to the wires followed a dispersive nature similar to blanket films. The relationship of such acoustic properties will be discussed in the context of the mechanical properties of the patterned structures and the influence of processing of the nanowires.

12:00pm **EM+AP+MS+NS+TF-ThM-13 Wafer-Scale Fabrication of Carbon-Based Electronic Devices*, Zhigang Xiao*, *J Kimbrough, J Cooper, K Hartage, Q Yuan,* Alabama A&M University

In this research, we report the wafer-scale fabrication of carbon nanotube or graphene-based electronic device such as field-effect transistors (FETs). Carbon nanotube-based devices were fabricated with the alternating electric field-directed dielectrophoresis (DEP) method, and the graphene-based devices were fabricated with the carbon films grown with plasma-enhanced atomic layer deposition (PEALD) or e-beam evaporation. Semiconducting carbon nanotubes were dispersed ultrasonically in solutions, and were deposited and aligned onto a pair of gold electrodes in the fabrication of carbon nanotube-based electronic devices using the dielectrophoresis method. The DEP-aligned tubes were further fabricated into carbon nanotube field-transistors (CNTFETs) and CNTFET-based electronic devices such as CNT-based inverters and ring oscillators using the microfabrication techniques. The fabricated devices were imaged using the scanning electron microscope (SEM) and high-resolution transmission electron microscope (HRTEM), and the electrical properties were measured from the fabricated devices using the semiconductor analyzer. The semiconducting CNTs achieved higher yield in the device fabrication, and the fabricated devices demonstrated excellent electrical properties.

Magnetic Interfaces and Nanostructures Division
Room A210 - Session MI+2D+AS+EM-ThM

Novel Magnetic Materials and Device Concept for Energy efficient Information Processing and Storage

Moderators: Mikel B. Holcomb, West Virginia University, Markus Donath, Muenster University, Germany

8:00am **MI+2D+AS+EM-ThM-1 Using Novel Magnonic Device Concepts for Efficient Information Processing*, Burkard Hillebrands,*** Technical University Kaiserslautern, Germany **INVITED**

In the field of magnonics, wave-based logic devices are constructed and studied based on the utilization of spin waves and their quanta - magnons. The field is developing rapidly due to its potential to implement innovative ways of data processing as a CMOS complementary technology. Basic building blocks of magnonics have already been realized. Examples are linear and nonlinear spin-wave waveguide structures, magnonic logic, as well as magnonic amplifiers such as the magnon transistor and parametric amplification.

In this talk, I will give an overview about the fundamentals and the current trends in magnonics. One topic is the realization of new functionalities and devices by using novel concepts borrowed from integrated optics and combining them with the specific advantages found in magnetic systems. Examples are directional couplers and quantum-classical analogy devices, such as a magnonic Stimulated Raman Adiabatic Passage (STIRAP) device.

Another important direction is to use fundamentally new macroscopic quantum phenomena such as a Bose-Einstein condensate (BEC) at room temperature as a novel approach in the field of information processing technology. Very promising is the use of magnon supercurrents driven by a phase gradient in the magnon BEC. I will demonstrate evidence of the formation of a magnon supercurrent along with second magnonic sound, and its spatiotemporal behavior, which is revealed by means of time- and wavevector-resolved Brillouin light scattering (BLS) spectroscopy. I will conclude with an outlook.

8:40am **MI+2D+AS+EM-ThM-3 Spin-Polarized Scanning Tunneling Microscopy of <10 nm Skyrmions in SrIrO3/SrRuO3 Bilayers*, Joseph Corbett*,** *J Rowland, A Ahmed, J Repicky,* The Ohio State University*; K Meng,* The Ohio State Univesity*; F Yang, M Randeria, J Gupta,* The Ohio State University

We imaged isolated <10 nm sized skyrmions in $SrIrO_3$ on $SrRuO_3$ by spin-polarized scanning tunneling microscopy. We fabricated bilayers of 2 unit cells of $SrIrO_3$ atop of 10 unit cells of $SrRuO_3$ via off-axis sputtering. This thickness combination was selected because it showed a strong topological hall signal. We observed a granular morphology of $SrIrO_3$ mounds with rare patches of exposed $SrRuO_3$. We can distinguish $SrIrO_3$ from $SrRuO_3$ by scanning tunneling spectroscopy where, $SrIrO_3$ grains show a gap-like feature, while $SrRuO_3$ have states near the Fermi level. The height histogram of the observed granular structures is consistent with an average of 2 unit cells of $SrIrO_3$. The grains of the $SrIrO_3$ appear to act as a nucleation for skyrmion formation. Similarly, we've imaged skyrmions under applied +/- 1 T fields demonstrating their magnetic character by observing an inversion in magnetic contrast. We found that the number of $SrIrO_3$ unit cells did not determine skyrmion formation, but the size of the skymrion was linked to the grain size, i.e. the skyrmion formed roughly the size of the grain. Furthermore, we've been able to manipulate the skyrmions by utilizing the influence of the tip. On-going investigations into the mechanism of the magnetic manipulation of the skyrmion are underway, as well theoretical modeling of the isolated skyrmion to ascertain the local Dzyaloshinskii-Moriya interaction constant.

9:00am **MI+2D+AS+EM-ThM-4 Relieving YIG from its Substrate Constraints - YIG Resonators on Various Crystalline Substrate Materials*, Georg Schmidt*,** Martin-Luther-Universität Halle-Wittenberg, Germany **INVITED**

We have recently demonstrated the fabrication of free-standing 3D yttrium iron garnet (YIG) magnon nano-resonators with very low damping [1]. At first the resonators were fabricated on gallium gadolinium garnet (GGG) substrates which are most suitable for epitaxial deposition of YIG. The process involves room temperature deposition and subsequent annealing. Transmission electron microscopy investigation of the bridge-like structures shows that the span of the bridge is almost monocrystalline while some defects nucleate at the transitions from the span to the posts of the bridge which are epitaxially bound to the substrate. This suggests that the quality of the span may only indirectly depend on the quality of the feet, the latter being largely determined by the lattice matching of the substrate material to the YIG. Being able to grow YIG structures on substrate materials other than GGG would not only be interesting because of availability and price but also because the high frequency properties of GGG are less than ideal while other materials like MgO or Sapphire would be preferred for high frequency applications. We have fabricated YIG bridges on various substrate materials including yttrium aluminium garnet (YAG), MgO, and sapphire. In most cases we achieve high crystalline quality of the span even for non-matching substrates. For some of the materials time resolved magneto optical Kerr microscopy even reveals magnon resonances with reasonable linewidth.

[1] F. Heyroth et al. cond-mat.1802.03176

9:40am **MI+2D+AS+EM-ThM-6 Magnetic Textures in Chiral Magnet MnGe Observed with SP-STM*, Jacob Repicky*,** *J Corbett, T Liu, R Bennett, A Ahmed,* The Ohio State University*; J Guerrero-Sanchez,* National Autonomous University of Mexico*; R Kawakami, J Gupta,* The Ohio State University

Materials with non-centrosymmetric crystal structures can host helical spin states including magnetic skyrmions. Bulk MnGe hosts a short period magnetic state (3 nm), whose structure depends strongly on atomic lattice strain, and shows a large emergent transport signature associated with the skyrmion phase. Here, we use low-temperature (5 K) spin-polarized scanning tunneling microscopy (SP-STM) to image the magnetic textures in MnGe thin films grown via molecular beam epitaxy and study the influence of the surface on those textures. Most microscopic locations show a spin spiral phase with a 6-8 nm period and a propagation direction that is influenced by step edges and surface termination. We also report the presence of isolated target skyrmions which have a triangular shape that appears to be set by the in-plane lattice vectors, and a core size of approximately 15 nm. We observe the target state is significantly more sensitive to magnetic fields than the spiral phase, and that local voltage and current pulses with the STM tip imply the texture can be 'switched' between states with different topological charge. Detailed analysis of atomic resolution STM images is used to probe the role of small lattice strain on the distinct textures. To fully understand the magnetic textures in MnGe we will expand this study by investigating films of different thicknesses to vary the magnetic anisotropy and strain.

Funding for this research was provided by the Defense Advanced Research Projects Agency Grant No. 18AP00008

11:00am **MI+2D+AS+EM-ThM-10 Dzyaloshinskii-Moriya Interaction in Magnetic Multilayers*, Hans Nembach,*** National Institute of Sandards and Technology (NIST) **INVITED**

The Dzyaloshinskii-Moriya Interaction (DMI) gives rise to chiral magnetic structures, which include chiral spin-chains and skyrmions. The latter have recently received much attention, especially for their potential application for magnetic data storage. Each skyrmion would represent a bit and would be moved along a racetrack. DMI requires broken inversion symmetry and can exist in the bulk as well as at interfaces, for example at interfaces between a ferromagnet and a material with large spin-orbit coupling like heavy metals. More recently it has been shown that interfacial DMI can also exist at interfaces with graphene and oxides.

We use Brillouin Light Scattering spectroscopy (BLS) to determine the DMI from the non-reciprocal frequency-shift Damon-Eshbach spin-waves. In order to gain deeper insight into the underlying physics of DMI, we prepared several sample series to study different aspects of the DMI. First, we prepared two samples series to study the relationship between the DMI and the Heisenberg exchange. One series was a $Ni_{80}Fe_{20}$ thickness series on a Pt layer and for the other series we introduced a Cu dusting layer at the interface between a CoFeB layer and Pt to disrupt the Heisenberg exchange directly at the interface. For both sample series, we found that the Heisenberg exchange and the DMI are proportional to each other as it has been predicted by theory. Next, we prepared a $Cu/Co_{90}Fe_{10}$ and a $Pt/Co_{90}Fe_{10}$ sample series, which were in-situ oxidized for different times and subsequently capped to prevent any further oxidation. Density functional theory calculations have shown that the hybridization and the associated charge transfer is important for the DMI and that interfaces with an oxide can have DMI. Our BLS measurements showed that oxide interfaces have DMI. Moreover, we showed that the spectroscopic splitting factor g, which we determined with ferromagnetic resonance spectroscopic, is correlated to the DMI. This is an indirect confirmation of the theory predictions regarding the role of hybridization and charge transfer.

So far, most work on DMI has been carried out for highly symmetric interfaces. Low symmetry systems can have anisotropic DMI and can potentially support anti-skyrmions. We prepared a Pt/Fe(110) sample and found that the DMI is anisotropic with the strongest DMI along the [001] direction, which coincides with the magnetic easy axis.

Finally, we studied the impact of He^+ ion irradiation on DMI for the Ta/CoFeB/Pt system. We found that the DMI increases with the dose before it drops for the highest does. This is in contrast to the perpendicular anisotropy, which continuously decreases with ion-irradiation.

11:40am **MI+2D+AS+EM-ThM-12 Transport in Goniopolar and (pxn) Metals*, Joseph Heremans,*** *B He, L Zheng, Y Wang, M Arguilla, N Cultrara, M Scudder, J Goldberger, W Windl,* The Ohio State University **INVITED**

semiconductors that have *p*-type conduction along some crystallographic directions and *n*-type conduction along others due to a particular topology of their Fermi surface. The electrical and thermoelectric transport of one member of this class, $NaSn_2As_2$, will be presented. A second class of materials have similar transport properties due to different mechanisms: some, like Be and Cd, have Fermi surfaces that contain both electron and hole pockets that have partial thermopowers of opposite polarities, but very anisotropic mobilities, so that one carrier type dominates the total thermopower in one direction, and the other carrier type dominates the thermopower in the other direction. A new member of this class, the semimetal bismuth doped p-type with Sn, will be described in this talks as well. In practice, a third class of artificial materials made of separate layers of p-type and of n-type semiconductors can be made to have a similar behavior in transport as well; the last two classes are called (pxn)-materials.

The electrical conductivity and thermopower tensors in goniopolar and (pxn) materials can be made to have off-diagonal components, which cause exciting new properties like zero-field Hall and Nernst-Ettingshausen effects. These materials can be used in single-crystal transverse thermoelectrics.

[1] He, B. et al , *Nat. Mater.* (published online doi.org/10.1038/s41563-019-0309, 2019)

[2] Zhou, C. et al. *Phys. Rev. Lett.* **110**, 227701 (2013).

Manufacturing Science and Technology Group
Room A226 - Session MS+EM+QS-ThM

Science and Technology for Manufacturing: Neuromorphic and Quantum Computing (ALL INVITED SESSION)

Moderators: Nathaniel C. Cady, SUNY Polytechnic Institute, Albany, Alain C. Diebold, SUNY College of Nanoscale Science and Engineering

8:40am **MS+EM+QS-ThM-3 Materials and Fabrication Challenges for Neuromorphic and Quantum Computing Devices***, S Olson, C Hobbs, H Chong, J Nalaskowski, H Stamper, J Mucci, B Martinick, M Zhu, K Beckmann, I Wells, C Johnson, V Kaushik, T Murray, S Novak, S Bennett, M Rodgers, C Borst, N Cady, M Liehr,* ***Satyavolu Papa Rao,*** SUNY Polytechnic Institute **INVITED**

Devices for quantum computing, quantum communications and quantum sensing share many challenges in terms of the materials, their interfaces, and fabrication technologies. This presentation will quickly review the broad swath of quantum technologies that are being actively studied, while identifying synergies among them that can be exploited for efficient development of integrated quantum computing systems. Advanced process tools capable of exquisite control of the processes, materials and interfaces at 300mm wafer scale have been utilized for the fabrication of structures for quantum computing. Examples of such efforts, including structures for superconducting transmon qubits, resonators, and superconducting nanowire single photon detectors, will be discussed – with an emphasis on the materials and process control issues that needed to be tackled, while keeping manufacturability considerations always in mind. The presentation will conclude with a discussion of how advances in the fabrication of such devices for quantum computing are being applied to ‘adjacent spaces’ such as neuromorphic computing using superconducting optoelectronics (in partnership with AFRL-Rome and NIST Boulder).

9:20am **MS+EM+QS-ThM-5 IBM Q: Quantum Computing in the 21st Century*, Robert Sutor,*** IBM Research **INVITED**

For almost 40 years, quantum computing has intrigued and amazed scientists and non-scientists in its future possibility for solving problems that are intractable using classical computing. Over the last three years, IBM has made real quantum computers available on the cloud so that clients, students, and researchers can begin to learn and experiment with this new way of computing. We'll see what use cases are being considered in industry, the state of quantum computing today, and how you can get on the right path to make the earliest use of this rapidly evolving technology.

11:00am **MS+EM+QS-ThM-10 Quantum Information Science at AFRL*, Michael Hayduk,*** Air Force Research Laboratory **INVITED**

Recent advances in Quantum Information Science (QIS) indicate that future applications of quantum mechanics will lead to disruptive advances in capabilities for the US Air Force. Controlling and exploiting quantum mechanical phenomena will enable inertial sensors and atomic clocks that provide GPS-like positioning and timing accuracy for extended periods of time in degraded environments, communications networks with information security based on physics principles, unprecedented sensor resolution, and computers that may be able to provide exponential speedup in processing speed. To ensure that the future Air Force warfighter maintains a technological advantage, the AF must implement a QIS strategy that leads to robust, deployable quantum systems. This invited talk will discuss the recently developed Air Force Research Laboratory QIS strategy that covers the areas of timing, sensing, communications and networking, and computing. Capability development across these four areas will also be discussed.

11:40am **MS+EM+QS-ThM-12 Neuromorphic Computing: From Emerging Devices to Neuromorphic System-on-a-Chip*, Vishal Saxena,*** University of Idaho **INVITED**

Several classes of emerging non-volatile memory (NVM) devices are currently being investigated for their application in analog implementation of artificial neural networks (ANN) hardware. The device can be two- or three-terminal and employ a wide range of material systems and associated physical mechanisms to achieve two or more non-volatile memory states. ANN hardware realizations include vector matrix multipliers (VMMs) and neural-inspired or Neuromorphic computing circuits. The NVM devices are employed in the form of crossbar or crosspoint arrays with or without selectors. In order to exploit the high-density and potential low-power operation of these devices, Analog circuit designers need to accommodate non-ideal behavior of these devices. This is particularly important for optimizing transistor-level circuit design for layout area, reliability, and static and dynamic power consumption. NVM nonidealities include device variability, low resistances offered by the two-terminal devices, finite resolution, relaxation of incremental states, limited dynamic range, and read/write endurance. This talk will provide an overview of Neuromorphic System-on-a-Chip (NeuSoC) that can be realized using emerging NVM arrays, expected device characteristics, associated circuit design challenges, and potential strategies for their mitigation. The talk will also include energy-efficiency estimation and benchmarking for NeuSoCs and provide pathways for future work in this area.

Thin Films Division
Room A122-123 - Session TF+EM+NS+SS-ThM

Thin Films for Energy Harvesting and Conversion

Moderators: Siamak Nejati, University of Nebraska-Lincoln, Xinwei Wang, Shenzhen Graduate School, Peking University

8:00am **TF+EM+NS+SS-ThM-1 Redesigning Batteries into Efficient Energy Harvesters and Sensors for Wearable Applications***, **Cary Pint,*** Vanderbilt University **INVITED**

Here I will discuss the research efforts of my team demonstrating how active materials utilized in batteries can be reconfigured into an electrochemical framework to harvest, rather than store, energy. This new functionality of battery materials arises from the fundamental coupling between mechanical stresses and electrochemistry that my group has demonstrated while investigating the “strain-engineering” of battery materials. By exploiting this coupling in a symmetric cell device configuration, we are able to construct devices that convert mechanical energy to electrical energy by mechanical modulation of the electrochemical reaction potential. I will discuss the development of this device platform from proof-of-concept device fabrication using 2D materials to our most recent demonstration of textile-integrated biocompatible fibers integrated into fabrics for harvesting/sensing of human motion. Most notably, I will discuss how the sluggish diffusion kinetics of ions between two electrodes – whereas a challenge for emerging battery applications, enables these devices to measure a continuous response from the whole broad range of frequencies associated with human motion. This allows these wearable harvesters to provide real-time sensing data that can be directly correlated with dynamic human motion models. This new approach leverages the efficient nature of electrochemistry, the wide range of materials selection and chemistries relevant for batteries, and without any of the safety concerns of batteries due to the symmetric electrode configuration.

8:40am **TF+EM+NS+SS-ThM-3 Engineering Effective Back Contact Barrier by interfacial $MoSe_2$ defect states for CZTSe: nanolayer Ge solar cells.***, **Sanghyun Lee,*** Indiana State University

The steadily emerging $Cu_2ZnSnSSe_4$ (CZTSSe) devices are alternative thin film solar cells with abundant elements in earth’s crust for the past several years. Despite several advantagessuch as high absorption coefficient ($>10^4$ cm^{-1}) and a tunable direct band gap energy (1 to 1.4 eV), the improvement and understanding have been stagnant in the past several years. Recently, CZTSe: nanolayer Ge solar cells have shown significantly improved pseudo-mono grain toward the depth direction.

Due to the improvement and the similarity between CZTSe and Cu(In,Ga)Se_2 (CIGS) thin film solar cells, the CZTSe/ Molybdenum (Mo) back contact interface was often misinterpreted by expecting the similar back contact property to CIGS. However, unlike the stable CISe ($CuInSe_2$)/Mo interface, the CZTSe/Mo interface is thermodynamically unstable due to the higher oxidation states of Sn. Although the presence of an interfacial $MoSe_2$ layer at Mo/absorber is always confirmed, properties of the back contact-interface such as structure and electrical behaviors are convoluted.

Following our empirical results about the back contact barrier of CZTSe: nanolayer Ge devices, we perform analytical and numerical modeling to explain the back contact improvement theoretically. The device modeling are carried out with the simulator, developed at Indiana State University. The tool is run in MATLAB environment, connected to other external tools (Sentaurus TCAD). Based on our result, defects in $MoSe_2$ interfacial layer dominate the back contact property of CZTSe: nanolayer Ge devices by increasing of the effective back contact barrier, which consists of two different back contact barriers, thereby increasing series resistance as well. The reduction of $MoSe_2$ defect concentration from 1 x 10^{17} to 1 x 10^{15} cm^{-3} decreases the effective barrier height by 51 meV, which results in approximately 34 % decrease in the series resistance (See supporting data). Conversely, as the defect concentration increases, the benefit from the back contact barrier lowering by the valence bands offset between $MoSe_2$ and CZTSe absorber is reduced and essentially eliminated. However, the back contact barrier between $MoSe_2$ and Mo metal contact remains the same even with increased $MoSe_2$ defect concentration. Incorporating thin Ge nanolayer at the interface between the absorber and $MoSe_2$ positively influences and possibly reduces the defect states, lowering the effective barrier. The exponential fitting of the effective barrier and series resistance agrees well with the experimental results. The improvement of the back contact barrier for CZTSe: nanolayer Ge devices is calculated as 23.8 meV than CZTSe without nanolayer Ge devices.

9:00am **TF+EM+NS+SS-ThM-4 Development of Low-Cost, Crack-Tolerant Metallization Using Screen Printing for Increased Durability of Silicon Solar Cell Modules***, O Abudayyeh,* Osazda Energy*; A Chavez,* University of New Mexico*; J Chavez,* Osazda Energy*; **Sang M. Han,*** University of New Mexico*; F Zimbardi, B Rounsaville, V Upadhyaya, A Rohatgi,* Georgia Institute of Technology*; B McDanold, T Silverman,* National Renewable Energy Laboratory

One of the ways to reduce the cost of solar electricity to 3¢/kWh, thus reaching parity with fossil-fuel-based generation, is to reduce the degradation rate of solar modules and extend their lifetime well beyond 30 years. The extended module lifetime in turn can positively influence the financial model and the bankability of utility-scale PV projects. Today, the highest-risk-priority solar module degradation mechanism is what is known as hot spots, often induced by cell cracks. In order to address this degradation mechanism, we make use of low-cost, multi-walled carbon nanotubes embedded in commercial screen-printable silver pastes, also known as metal matrix composites. When the carbon nanotubes are properly functionalized and appropriately incorporated into commercial silver pastes, the resulting metal contacts on solar cells, after screen-printing and firing, show exceptional fracture toughness. These composite metal contacts possess increased ductility, electrical gap-bridging capability up to 50 µm, and “self-healing” to regain electrical continuity even after cycles of complete electrical failure under extreme strain [1]. Accelerated thermal cycling tests on mini-modules constructed from aluminum back surface field (Al-BSF) cells show a slower degradation rate for the cells integrated with the composite grid fingers and busbars for the front surface metallization compared to the cells with conventional metallization.

[1] O. K. Abudayyeh, A. Chavez, J. Chavez, S. M. Han, F. Zimbardi, B. Rounsaville, V. Upadhyaya, A. Rohatgi, B. McDanold, T. J. Silverman, and N. Bosco, in "Low-Cost Advanced Metallization to Reduce Cell-Crack-Induced Degradation for Increased Module Reliability," 2019 NREL PV Reliability Workshop, Lakewood, CO, 2019.

9:20am **TF+EM+NS+SS-ThM-5 Fabrication of Optical Test Structures for Enhanced Absorption in Thin Multi-junction Solar Cells***, **Erin Cleveland,** N Kotulak, S Tomasulo, P Jenkins,* U.S. Naval Research Laboratory*; A Mellor, P Pearce,* Imperial College London, UK*; N Ekins-Daukes,* University of New South Wales, Australia*; M Yakes,* U.S. Naval Research Laboratory

In space applications, a key figure of merit is conversion efficiency at end-of-life, which combines both beginning–of-life efficiency with degradation due to radiation exposure on orbit. In currently used InGaP/GaAs/Ge triple junctions, the GaAs middle cell has the most pronounced degradation, which limits the total current generation at the end-of-life. Recently, we demonstrated that as the thickness of the GaAs cell decreases, the tolerance to radiation damage increases. [1] However, because the cell absorbs less light as the thickness of the active region is reduced, the beginning-of-life performance suffers as compared to optically thick cells. To realize the benefits of both structures, light trapping architectures may be used to increase absorption within the cell while still maintaining the increased radiation tolerance of the thinner geometry.

Designing a wavelength selective light trapping structure positioned interstitially between two of the subcells of a multi-junction device is a new challenge which prohibits many of the well-known light trapping techniques. Recently, we have proposed a structure which combines a distributed Bragg reflector (DBR) with a textured diffraction grating. [2] Such a structure would provide substantial absorption of light in the middle subcell of a multi-junction device, while still allowing enough low-energy light to pass through the structure so the bottom cell remains well current matched with the other junctions. This structure is proposed to have over an order of magnitude increase in overall radiation tolerance while maintaining comparable beginning of life performance to the current technology.

In this presentation, we present a first experimental demonstration of this structure. The design combines a diffraction grating fabricated via nanosphere natural lithography [3], a low-index transparent spacer layer, and a DBR, which synergistically traps light inside the targeted subcell. This presentation will highlight processing techniques and challenges associated with fabricating a textured ultra-thin solar cell, while illustrating the effectiveness of integrating light trapping structures within an ultra-thin solar cell as an effort towards realizing high efficiency ultra-thin photovoltaic devices.

[1] L. C. Hirst, *et.al*, “Intrinsic radiation tolerance of ultra-thin GaAs solar cells”, *APL*, 109 (2016)

[2] A. Mellor, N.P. Hylton, S.A. Maier, N. Ekins-Daukes, “Interstitial light-trapping design for multi-junction solar cells”, *Solar Energy Materials & Solar Cells*, 159, (2017)

[3] H.W. Deckman and J.H. Dunsmuir, “Natural lithography”, *Applied Physics Letters*, 41(4) (1982)

9:40am **TF+EM+NS+SS-ThM-6 Phosphorus as a *p*-Dopant in Pyrite FeS_2, a Potential Low-cost earth-abundant Thin Film Solar Absorber***, **Bryan Voigt**[1], W Moore, D Ray, M Manno,* University of Minnesota, Minneapolis*; J Jeremiason,* Gustavus Adolphus College*; L Gagliardi, E Aydil, C Leighton,* University of Minnesota, Minneapolis

Pyrite FeS_2 has long been considered an ideal absorber material for low-cost and sustainable thin film solar cells because it is composed of earth-abundant, non-toxic, inexpensive elements, has a suitable band gap (0.95 eV), and absorbs light so strongly that a 100-nm-thick film absorbs >90 % of photons with energies above the band gap. Lack of doping control, however, has presented a barrier to realization of the *p-n* pyrite homojunction, *i.e.*, the simplest route to a pyrite solar cell. *Heterojunction* pyrite solar cells have proven to have disappointingly low efficiencies (~3%), surface conduction and leaky surface inversion layers being implicated as the culprit. While mitigation of pyrite surface conduction remains a challenge, doping has begun to yield to understanding, renewing optimism for a *p-n* pyrite homojunction solar cell. In particular, we have shown that rigorously phase-pure pyrite single crystals and thin films are exclusively *n*-type, due to a common dopant. Most recently, we have identified sulfur vacancies as this unintentional *n*-dopant, enabling robust control over *n*-doping levels in single crystals grown by chemical vapor transport (CVT). Progressing towards a *p-n* pyrite homojunction, here we demonstrate effective *p*-type doping in crystals by introducing phosphorus in the vapor phase during CVT growth. Increasing the phosphorus concentration from <0.1 ppm to 30 ppm evolves electronic conduction from *n*-type to *p*-type, with a clear and reproducible majority carrier inversion for concentrations >10 ppm. Typical transport properties of phosphorus-doped, *p*-type pyrite crystals include a hole thermal activation energy, room temperature resistivity, hole density, and mobility of ~170 meV, 3 Ω cm, 2×10^{18} cm^{-3}, and 1 cm^2 V^{-1}s^{-1}, respectively. Density functional theory calculations confirm that phosphorus substituted on the S site is an acceptor, predicting a defect level at 200 meV above the valence band maximum, in good agreement with experiment. With both *n*- and *p*-type doping control achieved, attempts at *p-n* pyrite homojunction solar cells become possible.

This work was supported by the customers of Xcel Energy through a grant from the Renewables Development Fund and in part by the National Science Foundation through the University of Minnesota MRSEC under DMR-1420013.

11:00am **TF+EM+NS+SS-ThM-10 Relaxor-ferroelectric Thin Films for Energy Harvesting from Low-grade Waste-heat***, **Amrit Sharma**, B Xiao, S Pradhan, M Bahoura,* Norfolk State University

The need for efficient energy utilization is driving research into ways to harvest waste-heat which is ubiquitous, abundant and free. Thermal harvesting is a promising method for capturing freely available heat and converting it to a more usable form, such as electrical energy. Thermal harvesting for low power electronic devices using ferroelectric materials is one of the emerging areas of research because they possess spontaneous polarization and exhibit excellent piezoelectric as well as excellent pyroelectric coefficients. These materials are unique as they only sense time-dependent temperature change to generate electric power. We have grown lead-free $BaZr_{0.2}Ti_{0.8}O_3$ (BZT)/ $Ba_{0.7}Ca_{0.3}TiO_3$ (BCT) multilayer heterostructures and studied the structural, dielectric, ferroelectric, pyroelectric and energy density characteristics. The BZT/BCT multilayer epitaxial heterostructures were grown on SrRuO (SRO) buffered SrTiO (STO) single crystal substrate by optimized pulsed laser deposition technique. The large angle x-ray scans showed only diffraction peaks from the substrate and pseudocubic reflections (00*l*) from the multilayer heterostructure, confirming that these films are phase pure and epitaxial in nature. The atomic force microscopy (AFM) studies indicate that the surface roughness is low and that film growth is of high quality. The ferroelectric phase transitions have been probed above room temperature with relaxor behavior. The polarization versus electric field (P-E) measurement exhibits well-saturated hysteresis loop with maximum and remnant polarization of 138 and 64 µC/cm^2, respectively. Solid-state, thin-film devices, that convert low-grade heat into electrical energy, are demonstrated using pyroelectric Ericsson cycles, and their performance is optimized by independently enhancing pyroelectric coefficient and suppressing dielectric permittivity in compositionally graded heterostructures. Our findings suggest that pyroelectric devices may be competitive with thermoelectric devices for low-grade thermal harvesting.

11:20am **TF+EM+NS+SS-ThM-11 Thermal Treatment Effects on the Thermoelectric Devices from Sn/Sn+SnO_2 Thin Films***, **Satilmis Budak**, E McGhee, Z Xiao, E Barnes, R Norwood,* Alabama A&M University

Approximately two-thirds of energy is lost as waste heat; the direct harvest of this waste heat using thermoelectric (TE) materials has attracted worldwide interest. TE materials can convert waste heat from industrial processes, furnaces, and engine exhaust streams into useful electricity by the Seebeck effect. The energy conversion efficiency is shown by the dimensionless figure of merit, ZT, and $ZT=S^2\sigma T/K$, where S is the Seebeck coefficient, σ is the electrical conductivity, K is the total thermal conductivity, and T is the absolute temperature. The numerator $S^2\sigma$ defines the power factor (PF), which primarily relates to the electric properties [1]. When operating as an energy-generating device, the TE device is termed a thermoelectric generator (TEG). The source of thermal energy manifests itself as a temperature difference across the TEG. When operating in a cooling or heating mode the TE device is termed a thermoelectric cooler (TEC). Similarly, the TE device produces heating or cooling that takes the form a heat flux which then induces a temperature difference across the TEC. TE devices are solid-state mechanisms that are capable of producing these three effects without any intermediary fluids or processes. For power generation applications TE devices are used in automobiles as exhaust gas waste heat recovery devices where thermal energy is scavenged along the exhaust line of a vehicle and converted into useful electricity [2]. The TE devices from 50 alternating layers of Sn/Sn+SnO_2 thin films were prepared using DC/RF Magnetron Sputtering. They were heat treated at different temperatures to form nanostructures to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. Seebeck coefficient, van der Pauw resistivity, and thermal conductivity were used for the characterization. SEM/EDS was used to characterize the surface morphology of the films.

[1] Hongchao Wang, Wenbin Su, Jian Liu, Chunlei Wang, “Recent development of n-type perovskite thermoelectrics”, J Materiomics 2 (2016) 225-236

[2] Chetan Jangonda, Ketan Patil, Avinash Kinikar, Raviraj Bhokare, M.D.Gavali, “Review of Various Application of Thermoelectric Module”, International Journal of Innovative Research in Science, Engineering and Technology Vol. 5, Issue 3, (March 2016), 3393-3400.

Acknowledgement

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11:40am **TF+EM+NS+SS-ThM-12 Thermoelectric Properties of Efficient Thermoelectric Devices from Sb/Sb+SnO_2 Thin Films***, **Eshirdanya McGhee**, S Budak, Z Xiao, N Caver, B McNeal,* Alabama A&M University

The thermoelectric (TE) concept could be seen as a perfect solution for recovering waste heat from engine exhaust and converts in to electric energy. TE generators are all solid-state devices that convert heat into electricity. Unlike traditional dynamic heat engines, TE generators contain no moving parts and are completely silent. Such generators have been used reliably for over 30 years of maintenance-free operation in deep space probes such as the Voyager missions of NASA. TE systems can be easily

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[1] **TFD James Harper Award Finalist**

designed to operate with small heat sources and small temperature differences [1]. An ideal TE material behaves like an electron crystal and phonon glass, allowing a large temperature gradient across it while conducting electricity efficiently to generate a TE voltage. Significant progress in the TE performance of materials has been made by exploring ultra low thermal conductivity at high temperature and reducing thermal conductivity by nano-structuring, as well as by resonant doping and energy-dependent scattering of electrons [2]. The figure of merit ZT describes material performance. ZT depends on the thermoelectric material properties of Seebeck coefficient S, electrical conductivity σ, and thermal conductivity K, and ZT=S2σT/K where T is the temperature of the material [3]. TE devices from 50 alternating layers of Sb/Sb+SnO_2 thin films were prepared by DC/RF Magnetron Sputtering. TE devices were annealed at different temperatures to form nano-structures to increase the Seebeck coefficients and electrical conductivity and decrease thermal conductivity. For the characterization, Seebeck coefficient, van der Pauw resistivity, and thermal conductivity were used. The surface morphology was characterized using SEM/EDS.

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Acknowledgement

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12:00pm **TF+EM+NS+SS-ThM-13 3D Printed Triboelectric Nanogenerator**, *I Fattah, E Utterback,* ***Naga Srinivas Korivi****, V Rangari,* Tuskegee University

We report on the development of polymer nanocomposite layers made by 3D printing. The nanocomposite is composed of polydimethylsiloxane (PDMS), barium titanate nanoparticles, and multi-walled carbon nanotubes. Flexible layers of this composite have been 3D printed using a commercial 3D printer, and function as triboelectric energy generators. To the best of our knowledge, this is the first report of a PDMS based triboelectric nanogenerator fabricated by 3D printing. The nanogenerators have been evaluated in contact and separation mode and produce a maximum of 2.6 Volts under pressure from a human finger.

The fabrication procedure involves sonicating barium titanate ($BaTiO_3$, Skyspring Nanomaterials) and multi walled carbon nanotubes (MWCNT, Skyspring Nanomaterials) together in ethyl alcohol. This is followed by removing the excess ethyl alcohol, and manually grinding the nanoparticle powder to break any clusters. This is followed by mechanically blending liquid PDMS pre-polymer and its curing agent (~10:1 ratio by weight) with the nanoparticle powder in one beaker. Finally, the blend is filled into a dual plastic syringe, which is loaded onto an extrusion printing head of a commercial 3D printer (Hydra 16A, Hyrel LLC, USA). The printer reads a software file that defines the pattern or shape to be printed and dispenses the material from the syringe accordingly onto a base plate. For printing this composite, the base plate temperature was maintained between 75 – 90 °C, to allow curing within a few minutes. Once cured, the solid composite layers (270 µm thickness) can be peeled off the base plate.

The 3D printed PDMS-BaTiO3-MWCNT layers have been evaluated as triboelectric energy generation. In one embodiment, the 3D printed functions as the negatively charged layer in a contact-separation scheme. A polyimide sheet is used as positively charged layer. Carbon tapes are used as current collectors on both positive and negative charged layers. When these two layers are brought in contact with some pressure applied by a human finger, and then released, characteristic negative and positive voltage spikes are respectively observed. Peak voltages as high as 2.6 Volts have been obtained with the present 3D printed PDMS-BaTiO3-MWCNT layers. These observations indicate the applicability of this 3D printed composite in triboelectric energy generation.

Acknowledgments: This research was supported by the National Science Foundation grant #1827690.

Plasma Science and Technology Division
Room B130 - Session PS+2D+EM+SS+TF-ThA

Plasma-Enhanced Atomic Layer Etching

Moderators: Steven Vitale, MIT Lincoln Laboratory, Mingmei Wang, TEL Technology Center, America, LLC

2:20pm **PS+2D+EM+SS+TF-ThA-1 Atomic Layer Etch: Real World Utilization of an Idealized Solution***, **Peter Biolsi**,* TEL Technology Center, America, LLC **INVITED**

Atomic Layer Etch: Real World Utilization of an Idealized Solution

Critical dimensions (CD) continue to shrink driven by the quest for cheaper, faster and less power-consuming devices. If simple shrink was not enough, all of the back end, middle and front end of line (BEOL, MOL and MOL) also have introduced structural complexity and stringent topographic dimension, material property integrity and fundamental integration yield requirements. Atomic layer etching (ALE) has gained favor as an approach to extract more control over the fabrication of small CD complex topographic structures, atomic later etching. The idea is that alternating steps of self-limiting processes (e.g., passivation layer formation) and desorption (e.g., the removal of a passivation layer) mitigate aspect ratio dependence effects that lead to the aforementioned problems. The problem is that not all passivation processes are self-limiting. For the etching of dielectric materials, a self-limiting precursor step is not available as etch processes relies on cyclic process (fluorocarbon deposition and ion bombardment steps). Fluorocarbon based processes are not self-limiting rendering them quasi-atomic layer etch. Without special consideration, quasi-ALE has the same problems that continuous processes possess with additional burden of throughput.

Even though ALE can be difficult to be utilized in real-word scenarios, the learning from ALE finds its use in many etch applications. An etch chamber which can provide wide range of radical to ion flux ratios and precise ion energy control (using pulsing techniques) is suitable for ALE or utilizing ALE learnings. Currently, new ALE techniques based on surface modification by ions (Hydrogen plasma treatment of Silicon Nitride) followed by removal of modified layer by F radicals (High pressure NF3 or SF6 plasma) or surface modification by NH3/HF (to create a quasi-self-limiting diffusion barrier layer) followed by removal of modified layer by thermal means, are employed to etch critical layers where requirements are stringent. New frontier of etch technology will be the ability to achieve area selective etch without compromising etch rate of the process. Examples of such activities will be presented in this presentation.

3:00pm **PS+2D+EM+SS+TF-ThA-3 Mechanism of SiN Etching Rate Fluctuation in Atomic Layer Etching***, **Akiko Hirata**, M Fukasawa, K Kugimiya, K Nagaoka,* Sony Semiconductor Solutions Corporation, Japan*; K Karahashi, S Hamaguchi,* Osaka University, Japan

Atomic layer etching (ALE) enables atomic-precision control of the surface reaction and low damage etching of the underlying layer for device fabrication. In this study, we investigated SiN ALE with process optimization of the surface adsorption and desorption steps, and we clarified the rate fluctuation mechanism.

A dual frequency CCP reactor (60 MHz/2 MHz) was used in this study. A SiN (50 nm) was deposited on the Si substrate by LPCVD. One etching cycle consisted of two steps. CH_3F/Ar plasma was applied to deposit the hydrofluorocarbon (HFC) polymer as the adsorption step. Then, Ar plasma was used in the desorption step. The thicknesses of SiN and the HFC polymer were measured by spectroscopic ellipsometry. The chemical bonding was analyzed by XPS.

A 1.2-nm-thick HFC polymer was deposited on SiN as the adsorption step. Next, we investigated the desorption step by using Ar plasma. The etched amount for 1 cycle was 0.58 nm. However, we found the etch-stop of SiN after 10 cycles of ALE, owing to the deposition (>6 nm) of a protective film on the surface. The etch-stop could be caused by sputtering of the Si upper electrode and/or re-deposition of the HFC film. To investigate the etch rate fluctuation, the SiN surface after ALE was analyzed. C-C and C-N bonds were detected after 1 cycle, and C-C bonds increased after 10 cycles. It was clear that the excess HFC polymer deposition suppressed the ALE reactions. Ar^+ ion bombardment during the desorption step selectively eliminated the H and F in the HFC polymer, because the bonding energies of C-H and C-F were low. As the bonding energies of C-C (6.4 eV) and C-N (7.8 eV) are relatively high, these bonds remained after the desorption step. We speculated that excess C-rich polymer deposition after ALE started from the residual C-C bond. Residual Si-C bond is also possible reason, since the MD simulation revealed that the formation of Si-C bond was promoted in the fluorocarbon layer during SiO_2 ALE. [1] These results clearly showed that the initial adsorption kinetics of HFC polymer was strongly affected by the residual carbon on the SiN surface. To suppress the C-rich polymer deposition, we studied stable SiN ALE using the desorption step of Ar/O plasma (0.36 nm/cycle) and the two-step sequential desorption step of Ar and O plasma (0.6 nm/cycle). Although the effect of O adsorption in SiO ALE has been studied previously,[2] few studies have been reported for the case of SiN. Because the surface condition is able to fluctuate with the number of cycles, precise surface control is strongly required to achieve stable ALE.

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3:20pm **PS+2D+EM+SS+TF-ThA-4 Effect of Polymerization on Ar+ Bombardment Modification of SiO_2 and Si_3N_4 Substrates: Molecular Dynamics Simulation Study***, **Hojin Kim**, Y Shi, Y Tsai, D Zhang, Y Han,* TEL Technology Center, America, LLC*; K Taniguchi,* TEL Miyagi Limited, Japan*; S Morikita,* TEL Miyagi Limited*; M Wang, A Mosden, A Metz, P Biolsi,* TEL Technology Center, America, LLC

To understand the selective removal of silicon oxide (SiO_2) against silicon nitride (Si_3N_4) with gaseous reactants for advanced etch process, we have studied the surface modification of both SiO_2 and Si_3N_4 substrates with Ar+ bombardment by using molecular dynamics (MD) simulation. The substrate samples was prepared with and without carbon (C) and hydrogen (H) polymerization to investigate the effect of polymerization on surface modification. C and H atoms were deposited with low ion energy not to disrupt the surface much. After preparation of substrate, Ar+ bombardment with various ion energy (IE) were performed. We obtained a damage depth with a wigner-seitz defect analysis as a function of IE and compared the cases with and without polymerization to check the role of the added polymer layer on surface modification. In pristine Si_3N_4 and SiO_2 case, at IE=25eV, both substrates starts to show the damage with penetration of Ar+ and follows with an exponential raise as the IE increases. Damage depth at Si_3N_4 is deeper than that at SiO_2. In polymerization, simulations show that H is more deposited than C on Si_3N_4 while on SiO_2, C is more deposited than H. no silicon-hydrogen bonds appear on both substrates and in Si_3N_4, nitrogen-hydrogen bond is dominated while oxygen-carbon bond is popular in SiO_2. For damage analysis, in Si_3N_4 case, CH polymerization helps to lower about 30% in the damage depth with exponential behavior. However, SiO_2 case shows the opposite effect of CH polymerization in the damage depth. Formed polymer layer leads to increase the damage depth by comparing with pristine SiO_2 and helps more clear exponential behavior as a function of IE. Finally, analyzed results using XPS and/or SIMS from blanket SiO_2 and Si_3N_4 films etched in a Capacitively Coupled Plasma (CCP) chamber are compared with the MD simulation results.

4:00pm **PS+2D+EM+SS+TF-ThA-6 Advanced Cyclic Plasma Etch Approaches for Metal Patterning: Synergy and Surface Modification Effects***, **Nathan Marchack**,* IBM T.J. Watson Research Center*; K Hernandez,* University of Texas at Dallas*; J Innocent-Dolor, M Hopstaken, S Engelmann,* IBM T.J. Watson Research Center **INVITED**

Atomic layer etching or ALE is a burgeoning research area of plasma processing that offers critical advantages needed for future advancements in semiconductor devices, namely lower damage and enhanced selectivity, through its self-limited reaction cycles separated by purge steps.[1] ALE processes offer a significantly higher degree of tunability over traditional continuous-wave (CW) plasma etching, due to the fact that parameters such as gas flows, pressure, and bias power can be adjusted on a step-specific basis rather than as a global setting for the length of the process.

Our previous work investigated the effect of varying the purge step times in a quasi-ALE process using alternating Cl_2/H_2 exposures on the etched profiles of titanium and tantalum nitride.[2] Titanium and tantalum-based conductive films have been previously evaluated as gate materials for CMOS devices but more recently have been incorporated as top electrodes for novel technologies such as magnetoresistive RAM (MRAM) and hard masks for carbon electrodes utilized in biological sensing. As the trend of downscaling device size continues, the ability to pattern these films at tight pitches with minimal redeposition becomes highly important.

Sub-surface modification of films such as Si_3N_4 and indium-doped tin oxide (ITO) by low atomic weight (LAW) ions such as H^+ has been discussed in literature as facilitating self-limited etch behavior.[3,4] We present new data exploring the incorporation of LAW species into cyclic etch processes, namely penetration depth into these metal nitride films and their role in surface oxide formation, the latter of which can contribute to novel pitch multiplication schemes.[5] SIMS measurements reveal that the depth of penetration of H^+ for TaN films can be >40 nm and can occur through a native oxide layer that inhibits etching by Cl species. Pressure variation is a significant factor in tuning this effect, which can potentially modify the etch resistance of these films and enable novel integration schemes.

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4:40pm **PS+2D+EM+SS+TF-ThA-8 Surface Modification and Stability of Plasma-assisted Atomic-layer Etching (ALE) of Si based Materials; Analysis by Molecular Dynamics (MD) Simulation***, **Satoshi Hamaguchi**, M Isobe, E Tinacba, S Shigeno, Y Okada, T Ito, K Karahashi,* Osaka University, Japan

A plasma-assisted atomic-layer etching (ALE) process typically consists of alternating application of chemically reactive species (adsorption step) and Ar ion bombardment with low bias energy (desorption step) to the surface to be etched. In the adsorption step, a modified layer is formed on the material surface and, in the desorption step, the modified layer is removed with the original material underneath being intact. In this presentation, using the results of MD simulation of ALE for Si, SiO2, and SiN, together with experimental observations, physical mechanisms of the formation and removal of surface modified layers in typical ALE processes will be discussed.

Our molecular dynamics (MD) simulation of SiO2 ALE by fluorocarbon adsorption and Ar+ ion bombardment shows that preferential sputtering of oxygen takes place by Ar+ ion bombardment and a Si rich layer mixed with fluorine and carbon atoms is formed on the SiO2 surface. Ideally this modified layer should be removed completely in the subsequent desorption step, but in general it is not. In such a layer, the atomic number ratio of Si to O can be as high as unity and carbon provided in the subsequent adsorption step tends be deposited rather than removing O atoms from the surface by forming CO molecules. Therefore as the ALE cycles proceed, the adsorbed fluorocarbon layer thickens and eventually an etch stop may occur. With fine tuning of incident Ar+ ion energy, an etch stop may be avoided but the process window to achieve both continuous ALE cycles (by sufficiently high Ar+ ion energy) and ideal self-limit in each cycle (by sufficiently low Ar+ ion energy) may still be small or even nonexistent. The incompleteness of the modified surface removal in each ALE cycle seems universal phenomena for plasma-assisted ALE for most materials. For other plasma-assisted ALE processes that we examined by MD simulation, the surface modified layer formed during the adsorption step could not be removed completely by low-energy Ar+ ion bombardment, either. Indeed low-energy Ar+ ion bombardment contributes to the formation of a deeper modified layer by pushing down adsorbed species into the bulk, rather than simply removing it.

5:00pm **PS+2D+EM+SS+TF-ThA-9 Innovative Future Etch Technology by Atomic-order Control***, **Yoshihide Kihara**, T Katsunuma, S Kumakura, T Hisamatsu, M Honda,* Tokyo Electron Miyagi Ltd., Japan **INVITED**

In recent years, with the progress of device miniaturization and increased challenges in the scale of integration of semiconductor devices, ultra-high selectivity and atomic layer-level critical dimension (CD) control techniques are required in the fabrication processes.

In the conventional etching, using a fluorocarbon (FC) gas, the high selectivity is obtained by taking advantage of the difference of the FC protective film thickness due to the difference of materials.[1] However, adopting the conventional approach to cutting-edge pattern structure becomes difficult due to the excessive FC film clogging the micro slit facet. To meet the highly complex requirements, alternative process was developed by using ion modification and chemical dry removal.[2] We have made several improvements on this new approach and applied it to SiN and SiC etching. The improved new approach achieves ultra-high selectivity without FC protective film and we also confirmed this process has the characteristics of a self-limiting reaction based on ion depth profile as well as ALE.

In the patterning processes, lower pattern densities have a larger CD shrinking due to micro-loading. Hence, we developed the new process flow that combines atomic layer deposition (ALD) technique and etching. With this method, we achieved CD shrinking at atomic-layer level precision for various patterns, without causing CD loading.[3]

Moreover, Quasi-ALE can etch the pattern while maintaining the mask CD for different pattern density. This is because Quasi-ALE precisely controls the surface reaction by controlling the radical flux and ion flux independently.[3] Also, it was necessary to control oval CD size between X and Y respectively. We found that X-Y CD control can be easily performed by changing the balance of FC adsorption and Ar desorption in Quasi-ALE. However, there are concerns about mask selectivity and ion damage in this approach. To solve these problems, we introduce the Advanced Quasi-ALE technique which combines mask protection together with Quasi-ALE. The Advanced Quasi-ALE achieves wider X-Y CD control margin.

On the other hand, as aspect ratio is increased in the memory fabrication process, the occurrence of bowing profile is a serious problem. To address the issue, the new improvement technique has been developed that combines the concept of ALD and etching. With this method, we are able to etch profile more vertically in high A/R feature.

Reference

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Electronic Materials and Photonics Division
Room Union Station AB - Session EM-ThP
Electronic Materials and Photonics Poster Session

EM-ThP-1 Synthesis and Characterization of Fluorenone Derivatives as Organic Semiconductors for Organic Thin-Film Transistors*, **Sung Yong Seo**, J Jeong, K Lim, B Choi, Y Yun, M Son, G Kim,* Pukyong National University, Republic of Korea

Solution-processable 2,7-bis(5'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-*9H*-fluoren-9-one, 2-(2,7-bis(5'-(2-ethylhexyl)-[2,2'-bithiophen]-5-yl)-*9H*-fluoren-9-ylidene)malononitrile, 2,7-bis(5'-octyl-[2,2'-bithiophen]-5-yl)-*9H*-fluoren-9-one, and 2-(2,7-bis(5'-octyl-[2,2'-bithiophen]-5-yl)-*9H*-fluoren-9-ylidene)malononitrile were synthesized and characterized as solution-processable organic semiconductors for organic thin-film transistors (OTFTs). Thermal, optical, and electrochemical properties of the fluorenone-based semiconductors were investigated. The solution-sheared thin films based on fluorenone derivatives exhibited n and p-channel characteristics as an active layer in organic thin-film transistors according to the structure. The highest electron mobility was 0.085 cm^2 V^{-1}s^{-1}.

EM-ThP-2 Beryllium Oxide Band Alignment with Wide Bandgap Semiconductors*, **Donghyi Koh**, S Banerjee,* University of Texas at Austin*; J Brockman, M Kuhn, S King,* Intel Corporation

Beryllium oxide (BeO) is a large band gap (> 8 eV) dielectric with extreme properties that makes it ideal for pairing with other wide bandgap semiconductors with similar extreme properties for various high-power, -temperature, and -frequency device applications. For such devices to be succesful, large (> 1 eV) valence and conduction band offsets are needed at the interface between BeO and the wide bandgap semiconductor. However, relatively little is known regarding the band alignment between BeO and other materials. In this regard, we have utilized x-ray photoemission spectroscopy (XPS) to determine the valence band offset (VBO) between atomic layer deposited (ALD) BeO and epilayers of diamond and the cubic form of silicon carbide (3C-SiC) grown on silicon substrates. Using the valence band alignment rules of transitivity and commutativity, we are able to combine these results with previously reported values for the band alignment of BN, AlN, GaN, and InN to diamond and SiC to further deduce the alignment of these wide bandgap semiconductors to BeO. We will show that all BeO/wide band semiconductor combinations examined exhibit a type I band alignment with > 1 eV valence and conduction band offsets that are ideally suited for high-power, -temperature, and -frequency device applications.

EM-ThP-3 Thermal Conductivity of Nano-porous Low-k Dielectrics*, **Hari Harikrishna**, S Huxtable,* Virginia Tech*; S King,* Intel Corporation

We have investigated the influence of growth conditions, post deposition curing, and nano-porosity on the thermal conductivity for a series of organo-silicate (SiOCH) low-k dielectric thin films. Time-domain thermoreflectance (TDTR) was specifically utilized to meaure thermal conductivity while the influence of growth conditions and post deposition curing on mass density, network bond structure, percent porosity, pore size and pore interconnectivity were examined using techniques including nuclear reaction analysis (NRA), Rutherford backscattering spectroscopy (RBS), transmission Fourier-transform infrared (FTIR) spectroscopy, nuclear magnetic resonance (NMR), ellipsometric porosimetry (EP), and positronim annihilation lifetime spectroscopy (PALS). Analytical models describing the dependence of thermal conductivity on mass density and volume % porosity were found to generally over-predict the experimentally measured thermal conductivity, but improved agreement was obtained when considering only the density of heat carrying network bonds experimentally measured by FTIR. Ashby's semi-empirical relation, which assumes that only 1/3 of the heat carrying bonds are aligned to the heat transport direction, was also found to reasonably describe the observed trends relating thermal conductivity and mass density. However, the thermal conductivity results were found to be best described via a model proposed by Sumirat (*J. Porous Mater. 9, 439 (2006)*) which considers the effect of both the volume percent porosity and phonon scattering by nanometer sized pores.

EM-ThP-4 Characterization of Textile Yarn Coated with Polypyrrole/Carbon Black Electronic Material*, R Villaneuva, **Deepak Ganta**, C Guzman,* TAMIU

Electronic textiles combine the advantages of flexibility in textiles and the performance of electronics in a wearable form for sensing applications. We report an inexpensive and straightforward coating method of pre-treatment, dipping, and drying the cotton yarn, combining the advantages of polypyrrole/carbon black, while investigating the mechanical, in situ electrical properties, and thermal conductivity of polypyrrole/carbon black composite coated cellulose (cotton) yarn. The coated yarn is mechanically stable with the tensile strength of∼11.6 N. The resistivity and conductivity properties of the yarn are measured from the linear response of the I–V curve, showing an ohmic behavior. Further, the coated surface was tested using scanning electron microscopy for uniformity in the surface coating. Thermal conductivity for the coated fabric was measured using Transient-hot-bridge method and measured to be 0.12 Wm−1 K−1 at ambient temperature.

EM-ThP-5 Optical and Nonlinear Optical Properties of $(1-x)Pb(Mg_{1/3}Nb_{2/3})O_3\text{-}xPbTiO_3$ Thin Films Grown by Pulsed Laser Deposition*, **Da-Ren Liu**,* Taiwan Instrument Research Institute, Taiwan, Republic of Korea

Thin film optical devices have been especially attractive because of their potential for the integration with electronic and optoelectronic systems. Owing to its ferroelectricity, pyroelectricity, high dielectric constant and large electro-optic coefficients, lead magnesium niobate-lead titanate (PMN-PT) can be used in many applications that include pyroelectric detectors, actuators, integrated capacitors, and nonlinear optical devices. In this study, highly textured thin films of lead magnesium niobate-lead titanate were grown by pulsed laser deposition (PLD). The measurement of glancing-angle x-ray powder diffraction (GAXRD) was used to determine the structure of the PMN-PT films. The thickness and roughness of the films were characterized by grazing-incidence x-ray reflectivity (GIXR), and the complex refractive indices were measured in the range from 1.5 to 4.1 eV by spectroscopic ellipsometry (SE). The average oscillator strength and its associated wavelength were estimated by using a Sellmeier-type dispersion equation. Z-scan measurements were performed to study the third-order optical nonlinearity. It was found that the PMN-PT films exhibited strong nonlinear optical effect. The results show that PMN-PT thin films are promising materials for nonlinear optics.

EM-ThP-6 Toward Selective Deposition of Boron Carbide Layers*, **Raja Sekhar Bale**, R Thapa, L Dorsett, S Wagner, D Bailey, A Caruso,* University of Missouri-Kansas City*; J Bielefeld, S King,* Intel Corporation*; M Paquette,* University of Missouri-Kansas City

The semiconductor industry is pushing its boundaries in device scaling technology by way of novel processing methods and increasingly complex patterning schemes. This requires a variety of functional and patterning-assist materials as well as advanced deposition techniques. For years, Si-based materials have been used to meet these needs; however, these alone cannot fulfill the range of material requirements moving forward. Boron carbide has shown promise due to compelling dielectric, thermal, mechanical, chemical, and etch properties. Toward applying this material to next-generation integration schemes, we have been exploring the potential of going beyond traditional growth processes (e.g., plasma-enhanced chemical vapor deposition) and investigating innovative area-selective atomic layer deposition (AS-ALD) strategies. Herein we explore schemes for the selective metal/dielectric deposition of boron carbide using layer-by-layer methods. X-ray photoemission spectroscopy (XPS) and atomic force microscopy (AFM) techniques are employed for characterization and imaging of the resulting surfaces.

EM-ThP-7 The Effect of Processing Conditions on the Growth of Transition Metal Dichalcogenides by Molecular Beam Epitaxy*, **Peter Litwin**, S McDonnell,* University of Virginia

The synthesis of high-quality transition metal dichalcogenides films is of significant interest for potential applications in nanoelectronic and thermoelectric devices. Molecular beam epitaxy is a promising route towards this aim, providing fine control over growth conditions. To further the present understanding of growth conditions on the quality of transition metal dichalcogenide thin films, we study the effect of growth temperature, chalcogen to metal flux ratio, and the use of a ripening step on the stoichiometry and surface morphology of grown WSe$_2$ thin films. In-situ X-ray photoelectron spectroscopy is performed to analyze the intrinsic chemical composition of the grown material prior to atmospheric exposure, and ex-situ atomic force microscopy is employed to study the surface morphology of grown, sub-monolayer films. We find that both low and high growth temperature ranges can be detrimental to the chemical makeup of the grown material and that these results are echoed in the resulting grain morphology. An intermediate growth temperature produced chemically superior films over a wide range of chalcogen to metal flux ratios. The chalcogen to metal flux ratio was seen to provide some control of the film morphology, with high fluxes producing films with cleaner grain boundaries. Lastly, we show that the use of a ripening step in the early stages of growth results in a chemically superior material. This ripening step has the added benefit of producing films which are chemically more consistent than those grown in the absence of this step. There is also evidence to suggest that utilizing a ripening step may expand the processing window for film growth, allowing the use of higher processing temperatures and consequently better control over film quality.

EM-ThP-8 Co-sputtered and Rapid Thermal Annealed ZnS:Cu Thin Films for Photovoltaic Applications*, Y Jun,* EM Co., Inc., Republic of Korea*; **Sakal Pech**, M Yoo, G Cho, N Kim,* Chosun University, Republic of Korea

ZnS is one of the attractive II-VI semiconductors because of their potential applications in the novel electronics and optoelectronics devices. ZnS is an n-type semiconductor with relatively high transparency, large Bohr exciton radius (2.5 nm), large exciton binding energy (40 meV), high index of refraction (2.27) [1], and wide bandgap showing different bandgaps of 3.68 eV and 3.91 eV for cubic zinc blende (ZB) phase and hexagonal wurtzite (WZ) phase, respectively [2]. ZnS is considered one of the prospective candidates for the CIGS photovoltaic (PV) applications, compared to CdS, it has non-toxic handling, wide bandgap, and better lattice matching to CIGS absorber with bandgaps of 1.3–1.5 eV [2]. Some dopant metals, such as Al, Cu, Ag, Mn, and Tb, are widely doped into ZnS lattice. Some researchers have studied the effect of Cu doping on the emission of light in ZnS, in this study, ZnS:Cu thin films were deposited by using a co-puttering method for photovoltaic applications. Effect of doping content on morphological, optical and electrical properties of ZnS thin films after rapid thermal annealing (RTA) treatment was investigated with the structural properties of the different phases of ZB, WZ, and the mixture of them in X-ray diffraction studies . Optical and electrical characteristics of the thin films were analyzed by using an UV-Visible spectrophotometer and a Hall effect measurement system for optical transmittance, bandgap, resistivity, and carrier concentration. Acknowledgement: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20184010201650). [1] Sanjeev Kumar, C.L. Chen, C.L. Dong, Y.K. Ho, J.F. Lee, T.S. Chan, R. Thangavel, T.K. Chen, B.H. Mok, S.M. Rao, M.K. Wub, Room temperature ferromagnetism in Ni doped ZnS nanoparticles, J. Alloy Compd. 554, 357 (2013). [2] Md. Anisuzzaman Shakil, Sangita Das, Md. Ashiqur Rahman, Umma Salma Akther, Md. Kamrul Hassan Majumdar, Md. Khalilur Rahman, A Review on Zinc Sulphide Thin Film Fabrication for Various Applications Based on Doping Elements, Mater. Sci. Appl. 9, 751 (2018).

EM-ThP-9 Biomimetic Electrospun Polyethylene Fabrics for Effective Radiative Cooling Under Sunlight*, **Bokyung Park**, S Han, S Han,* University of New Mexico

Clothing fabrics normally show high absorptivity for the mid-infrared radiation from human body. This high absorptivity, compared to transparency in the same spectral region, makes heat removal from the body relatively inefficient in hot weather conditions. In addition, the microstructures of typical fabrics are far from optimum for effective light scattering in the visible range, and the absorbed sunlight can significantly heat up the skin under the fabric. In this work, we borrow our inspiration from nature to optimize the fabric design. Biological species, such as white beetles, ingeniously regulate their body temperature using their scales. These scales consist of anisotropic fibrillar network structures to achieve extraordinary light scattering that is far superior to man-made optical diffusers. Based on the random photonic structures found in beetle scales, we have electrospun biomimetic fabrics using polyethylene, which is minimally absorptive in the mid-infrared range. By manipulating the fabric microstructures (e.g., anisotropy, porosity, and fibril diameter), we were able to increase the sunlight scattering strength. Optical scattering strength of our fabrics was characterized, using the optical diffusion model where the minimum photon transport mean free path – a length over which light propagation is no longer correlated to its original direction – represents the maximum scattering strength . We have discovered that the scattering strength can be enhanced by almost a factor of two by increasing the anisotropy of threads in the fabric. Our results suggest that fabrics for efficient heat removal from human body can be fabricated by simple electrospinning techniques that are low-cost, scalable, and high-throughput.

EM-ThP-10 Suppression of the Spectral Weight ofTopological Surface States on the Nanoscale via Local Symmetry BreakingviaLocal Symmetry Breaking*, **Omur E. Dagdeviren**, S Mandal, K Zou, C Zhou, G Simon, S Albright, X Zhu, S Ismail-Beigi, F Walker, C Ahn, U Schwarz, E Altman,* Yale University

In topological crystalline insulators, the topological conducting surface states are protected by crystal symmetry. Here, we show using scanning tunneling microscopy/spectroscopy that defects that break local mirror symmetry of SnTe suppress electron tunneling over an energy range as large as the bulk band gap, an order of magnitude larger than that produced globally via magnetic fields or uniform structural perturbations [1]. The results reveal the influence of various defects on the electronic properties, including screw dislocations, point defects, and tilt boundaries that lead to dislocation arrays that serve as periodic nucleation sites for pits grown on SrTiOinsulators the topological conducting surface states are protected by crystal symmetry. Here, we show using scanning tunneling microscopy/spectroscopy that defects that break local mirror symmetry of SnTe suppress electron tunneling over an energy range as large as the bulk band gap, an order of magnitude larger than that produced globally via magnetic fields or uniform structural perturbations [1]. The results reveal the influence of various defects on the electronic properties, including screw dislocations, point defects, and tilt boundaries that lead to dislocation arrays that serve as periodic nucleation sites for pits grown on $SrTiO_3$ [2,3]. Complementary ab initio calculations show how local symmetry breaking obstructs topological surface states as shown by a threefold reduction of the spectral weight of the topological surface states. The findings highlight the potential benefits of manipulating the surface morphology to create devices that take advantage of the unique properties of surface states and can operate at practical temperatures.

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[3] O.E. Dagdeviren et al., Physical Review B **93**, 195303 (2016).

EM-ThP-11 Optical and Electrical Properties of Layer-by-layered and Mixed ZnS/CdS Structures with a Decrease in Cd-content by Co-sputtering Method*, S Pech,* Chosun University, Republic of Korea*; Y Jun,* EM Co., Inc., Republic of Korea*; **Geum-Bae Cho**, N Kim,* Chosun University, Republic of Korea

CdS is one of the most attractive n-type II–VI semiconductor materials for window layers or buffer layer in heterojunction thin film solar cells because of its high transmitivity, low resistivity, and excellent permeability with a bandgap of 2.42 eV [1]. However, the use of cadmium would be deleterious for the environment because of carcinogenic and toxic nature. To reduce the use of cadmium ZnS/CdS structures were investigated in this study. ZnS is an n-type semiconductor with relatively high transparency, large Bohr exciton radius (2.5 nm), large exciton binding energy (40 meV), high index of refraction (2.27) [2]. Two types of structure were fabricated with the same thickness: layer-by-layered and mixed structures were fabricated by co-sputtering method with each ZnS and CdS target as a function of Cd-content. Cd-content was adjusted by a sputtering time for CdS target. All samples were annealed in a rapid thermal annealing system at 400°C for 10 min. Structural properties of two-types of structure with the different Cd-content by X-ray diffraction studies. Optical and electrical properties of them were analyzed by using an UV-Visible spectrophotometer and a Hall effect measurement system for optical transmittance, bandgap, resistivity, carrier mobility, and carrier concentration. Acknowledgement: This work was supported by the Korea Institute of Energy Technology Evaluation and Planning (KETEP) and the Ministry of Trade, Industry & Energy (MOTIE) of the Republic of Korea (No. 20184010201650). [1] Nam-Hoon Kim, Seung-Han Ryu, Hyo-Sup Noh, Woo-Sun Lee, Electrical and optical properties of sputter-deposited cadmium sulfide thin films optimized by annealing temperature, Mater. Sci. Semicond. Process. 15, 125 (2012). [2] Sanjeev Kumar, C.L. Chen, C.L. Dong, Y.K. Ho, J.F. Lee, T.S. Chan, R. Thangavel, T.K. Chen, B.H. Mok, S.M. Rao, M.K. Wub, Room temperature ferromagnetism in Ni doped ZnS nanoparticles, J. Alloy Compd. 554, 357 (2013).

EM-ThP-12 Design and Simulation of a Leaf-like Antenna on Thin Kapton Sustrate for the 915MHz Frequency*, **Felipe Frazatto**, L Manera, L Perissinotto,* UNICAMP, Brazil

When launching a satellite into orbit, every gram reduced from its total weight counts toward cheaper missions, with this in mind and inspired by the wide range of applications allowed by flexible electronics, this work presents the study and simulation of a leaf-like coplanar microstrip antenna on an one mil thick Kapton substrate centered in the 915MHz frequency to be used with a LoRa communication module in Low Earth Orbit (LEO) CubeSats.

Ring resonators and coplanar transmission lines (CPW) were also simulated to be used in the substrate's material characterization and help understand the various challenges poused by the thin thickness. Comparing the simulations of the CPW and characteristic impedance equations found in the literature, it was possible to notice divergences between the simulated model impedance and the theoretical calculated value when dealing with the thin substrate, witch indicates that the equation's models may not consider effects that appear with the reduced thickness, making it difficult to obtain a good impedance matching.

The designed antenna is presented alongside a impedance matching semi flexible circuit, a coplanar waveguide, ring resonator and the study of the impedance matching hardships when using thin substrates for radio frequency applications.

EM-ThP-13 Atom Probe Tomography Analysis of the Composition of GaAsNBi, ***Jared W. Mitchell***, *R Goldman,* University of Michigan, Ann Arbor

We use atom probe tomography (APT) to develop an understanding of the composition of our $GaAs_{1-x-y}N_xBi_y$ samples. These alloys are of interest because of the significant bandgap narrowing that can be generated by incorporation of dilute concentrations of N and Bi. Notably lattice-matching with a GaAs substrate has also been demonstrated, yielding a bandgap of ~1 eV with a ratio of x_N/y_{Bi} = 083. The distribution of these alloys in the sample is of marked interest because of the observation of localized states generated by their incorporation, notably in the case of interstitial complexes developing in the As sublattice, which are important contributors to the electronic structure of these materials. We use APT to demonstrate the presence of As cluster states and to evaluate the composition and distribution of impurities of our sample.

EM-ThP-14 Silicon Nanowire P-N Junction Photovoltaic Device, ***Michael Small***, *S Collins, R Smith,* University of Maine

This paper presents the fabrication and testing of a low cost, silicon nanowire photovoltaic device. The silicon nanowires are etched into the surface of a silicon wafer, via metal assisted chemical etching (MACE). This method of nanowire fabrication does not require photolithographic patterning, thereby reducing manufacturing complexity and related costs. Vertically aligned nanowire p-n junctions have the potential to increase the optical bandwidth of a silicon photovoltaic device by allowing a greater amount of short wavelength light to reach the depletion region near the junction, resulting in improved conversion efficiency. When compared to a planar analog, the nanowire device produced an order of magnitude higher power in response to blue light (405 nm), attributed to increased collection at the exposed p-n junctions. Power conversion efficiency is eight times better than previously reported with a similar construct.

EM-ThP-15 Effect of N_2/H_2 Plasma on the Epitaxial Growth of InN by Hollow Cathode Plasma Assisted Atomic Layer Deposition, ***Mustafa Alevli***, *N Gungor,* Marmara University, Turkey

The high electron saturation velocity, small effective electron mass and high electron mobility of indium nitride (InN) makes it a suitable material for high frequency electronics. The possibility of InN in the existing high electron mobility transistors (HEMTs), currently based on other group III-nitrides. However, InN decomposes to In metal and N_2 gas at around 500°C, making deposition of the InN films challenging with conventional methods such as metal organic chemical vapor deposition (MOCVD) and Molecular Beam Epitaxy (MBE). Nevertheless, Hollow cathode plasma assisted atomic layer epitaxy (HCPA-ALD) is a layer-by-layer crystalline growth technique that is based on a pair of self-terminating and self-limiting gas-surface half-reactions, in which at least one half-reaction involves species from plasma. The inclusion of plasma generally offers the benefit of substantially reduced growth temperatures and greater flexibility in tailoring the gas-phase chemistry to produce varying film characteristics. The benefits of plasma come at the cost of a complex array of process variables that often challenge the ability to predict, a priori, the influence of any one input parameter. This work focuses on a variety of gas input flow fractions (N_2 and N_2/H_2) used in the HCPA-ALD growth of InN films. Changes in plasma parameters are then linked with changes in film characteristics. To evaluate the optical properties of the InN films, we use spectroscopic ellipsometer to measure the dielectric function and a complex refractive index. Data were fitted using a fitting based analysis program, and the results show our films have a bandgap of about 1.4 eV, which is bigger than the previously reported values. The Raman spectra showed two Raman active modes of E_2 and A_1(LO) of the wurtzite InN for all InN samples. For InN, we found out that addition of H_2 plasma with N_2 plasma resulted in InN films with poor crystalline quality showing high level of impurities with significant voids in the films, resulting in low-density films with poor adhesion properties. Our results indicate that higher N_2 plasma exposure time is necessary to obtain InN films with minimum amount of carbon incorporation. The presence of C impurities was observed in all films grown with N_2 plasma only and suggests that the N_2 plasma without H_2 is not efficient in terms of effectively removing the ligands of the chemisorbed organometallic trimethyl-metal precursors.

EM-ThP-16 Atomic Layer Deposition of Functional Films for Transparent and Flexible Organic Electronic Devices, ***Yu Duan***, Jilin University, China

Among the advanced electronic devices, transparent flexible organic electronic devices with rapid development are the most promising technologies to customers and industries. However, thin-film encapsulation (TFE) and the transparent oxide conductive (TOC) of organic devices still remain a big challenge, because of the difficulty in low temperature and low plasma power fabricating process. Atomic layer deposition (ALD) is increasingly used in the field of organic electronics. However, the deposition of ALD outside the temperature window still cannot be stably implemented. In this study, transient steric hindrance caused by gas-phase molecules at low-temperature (80℃) was investigated. In order to mitigate the effect of this transient hindrance, a process of consecutive short-pulses was adopted in fabricating TFE and TOC. Overall, the proposed idea would help low-temperature ALD for organic electronics become mature and be widely promoted.

EM-ThP-18 Incredibly Simple Synthesis of a Zinc Oxide / Graphene Hybrid Nano Material, ***Daniel Little***, Ohio Dominican University; *J Pfund, A McLain, S Lantvit, S King,* University of Wisconsin - La Crosse

Hybrid materials of zinc (II) oxide (ZnO) nanocrystals and graphene are of current interest due to their cheap, Earth-abundant composition, low toxicity, and varied applications in photocatalysis, sensing, and electronics among others. We have developed a novel methodology for the synthesis of such materials utilizing the thermal decomposition of zinc (II) oxalate in solid-state solution with graphene nanoplatelets. Although the procedure involves simply precursor mixing and heating, electronic interaction between the ZnO and graphitic phases is spectroscopically observed in the hybrid material – beyond that of a homogeneous mixture of ZnO and graphene – via powder XRD, XPS, and ATR-IR spectroscopy. The synthetic method employed can be easily tuned for the desired hybrid product stoichiometry, and is easily industrially scalable with minimal chemical waste products. The method can also be adapted for the creation of thin film composite materials.

EM-ThP-19 Metal Oxide-based Heterojunction Thin Films for Solar Cell Applications, ***Zainuriah Hassan***, *M Mohamed Saheed, A Yusof,* Institute of Nano Optoelectronics Research and Technology (INOR), Universiti Sains Malaysia, 11800 USM, Penang, Malaysia

Hello Everyone,

I'm writing on behalf of Pete Sheldon and Joe Greene to advise you that we will have a brief Executive Session on Monday, July 29th, from 7:30 – 8:15 a.m. just prior to the Board Meeting, in the New York Office—the agenda is attached. Please plan accordingly!

We look forward to seeing you in New York!

Yvonne

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